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STUDY OF SELF-ADHESION AND BIODEGRADATION OF BIODEGRADABLE POLYMER FILMS

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DEDICATION

"To my beloved family"

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RÉSUMÉ

La nécessité criante de surmonter les problématiques liées à la fin de vie des films de plastique à base de pétrole utilisés dans l'industrie de l'emballage présente une opportunité unique d'évaluer le potentiel des plastiques bio-sourcés et biodégradables comme alternatives viables aux plastiques à base de pétrole. Les films de plastique en tant qu'emballages multicouches ont différentes fonctions telles que la résistance au transfert de l'oxygène, la vapeur d'eau et la perte d'arômes. On réfère à ces propriétés en tant que propriétés "barrières". Les performances de l'emballage dépendent également de certaines propriétés mécanique, thermique et chimique. Une fonction essentielle pour tout emballage hermétique, est fournie par une couche dénommé la couche de scellant. Cette couche garantie un scellage hermétique, qui assure sa performance au niveau des propriétés barrières.

Le choix du matériau biodégradable pour la couche de scellant est un défi de taille et constitue un des focus principaux de cette thèse. Le manque de revues de littérature sur les propriétés de scellage et du comportement d'auto-adhésion des résines biodégradables est un problème considérable. De plus, la présence d'un choix limité de résines faisant partie de la classe des bioplastiques fait en sorte qu'il est nécessaire d'effectuer une quantité immense de tests préliminaires avec pratiquement toutes les résines accessibles. Le choix du matériau pour la couche de scellant a été effectué suite à l'évaluation préliminaire de plus de dix plastiques biodégradables différents. Les propriétés de ces matériaux ont des limitations au niveau de la ténacité, de la stabilité thermique et d'une cristallinité élevée. Conséquemment, la transformation et l'extrusion de ces matériaux requièrent des précautions extrêmes, puisque ces résines biodégradables sont susceptible à la dégradation thermique lors de la transformation à l'état fondu.

Le Polylactide (PLA) est une résine bio-sourcée commercialement disponible avec de bonnes propriétés mécaniques et dont il est possible de contrôler la structure moléculaire lors de sa production. Les PLA disponibles sur le marché sont catégorisés dans deux groupes: le cristallin et l'amorphe. Suite à l'étude initiale, il est évident que le PLA amorphe possède le meilleur comportement lors du scellage à chaud. Cette résine a donc été sélectionnée comme matériau principal pour la suite des travaux.

Les bioplastiques disponible commercialement, en tant que résines pures, ne peuvent répondre aux exigences d'une couche de scellant pour une application d'emballage. C'est

pourquoi des modifications subséquentes sont nécessaires. Dans le cas particulier du PLA, sa fragilité est un désavantage important. Une ténacité accrue peut être atteinte par le mélange à l'état fondu du PLA avec d'autres polymères de type élastomère, e.g. le caoutchouc naturel, les polyesters aromatiques, les copolyesters aromatiques, les polyoléfines, etc..

Le Poly-ε-caprolactone (PCL) et le Poly(butylène adipate-co-terephthalate) (PBAT) ont été sélectionnés comme représentant du groupe des polyesters aliphatique linéaires et des copolyesters aromatiques, respectivement. Ces deux polymères ont été utilisés afin de modifier les propriétés mécaniques et le comportement du scellage à chaud de la résine de PLA.

L'amélioration simultané des propriétés de scellage via l'utilisation de mélanges de résines biodégradables est un autre focus de cette thèse. La modification du comportement de biodégradation de ces résines due à leur mélange est également étudiée, afin de déterminer si l'emballage peut toujours être considéré comme étant compostable.

Initialement, dans le but de démontrer l'efficacité du mélange à améliorer les propriétés précédemment mentionnées; des mélanges renforcés de Poly(acide lactique) (PLA) et de Poly-ε-caprolactone (PCL) ont été investigués et comparés aux résines pures en terme de comportement mécanique et de leur performance au niveau du scellage. Tous les échantillons utilisés sont des films ayant une épaisseur de 35 μm, produit par extrusion au travers d'une filière plate. La morphologie des mélanges est affectée par l'écoulement en élongation présent dans la filière plate et une morphologie laminaire en résulte pour les mélanges de 20% et 40% de PCL. Il est démontré que la cristallinité des mélanges est affecté par la faible mobilité des chaînes moléculaires du PLA. Ceci résulte en des mélanges ayant d'avantage de phase amorphe. Jusqu'à 30^{o}C de réduction des températures d'initiation pour le thermo-scellage et de la tenue à chaud a d'ailleurs été observé pour les mélanges comparativement au PLA pur. Toutefois, tous les échantillons avaient une température d'initiation supérieure à la température de fusion du PCL. Une augmentation de la force de tenue à chaud des mélanges, atteignant 1700g/25,4mm pour une teneur de 40% de PCL montre une amélioration significative de l'auto-adhésion des échantillons mélangés. Les propriétés mécaniques des mélanges sont également significativement affectées par le mélange à l'état fondu: une plus grande élongation à la rupture et une plus grande ténacité rendent ces mélanges moins susceptibles aux défauts causés par la manutention et le stockage.

Le PCL est un polyester aliphatique relativement coûteux qui possède une temperature de fusion et une température de ramollissement assez basses. Ces caractéristiques entraînent un coût

de production élevé, en plus d'engendrer des problématiques au niveau de la manutention et du stockage dans les régions arides. Il existe des alternatives au PCL, tel que le PBAT, qui fait partie des copolyesters aromatiques et qui possèdent une température de fusion plus élevée, avoisinant 120^{o}C. Ses coûts de production sont également plus faible. L'utilisation d'une résine ayant un point de fusion élevé pour la modification des propriétés du PLA nécessite une étude approfondie sur la cristallinité et ses effets sur le comportement de ces résines lors du scellage à chaud.

Afin d'apporter une compréhension approfondie des effets du mélange, nous avons subséquemment utilisé le Poly(acide lactique) (PLA) amorphe et ses mélanges avec le Poly(butylène adipate-co-terephthalate) (PBAT). L'avantage de ce mélange est le point de fusion du PBAT plus élevé que la température d'initiation de la tenue à chaud du PLA. Les mélanges de PBAT et PLA amorphe offrent la possibilité d'analyser l'effet du changement de la structure cristalline sur la température d'initiation de la tenue à chaud. En utilisant des films de PBAT ayant subi une trempe comme référence, il a été démontré que la structure cristalline du PBAT a un effet significatif sur la température d'initiation de la tenue à chaud (T_{si}), causant jusqu'à 20^{o}C d'écart sur cette propriété. L'incorporation du PBAT comme phase dispersée diminue la teneur cristalline du PBAT, ce qui modifie également la T_{si} des mélanges. Dans ce cas, la même morphologie que les mélanges précédents a été obtenue, à cause du rapport des viscosités près de l'unité et du champ d'écoulement en élongation du procédé d'extrusion en filière plate. Un facteur de forme élevé de la phase dispersée est un atout facilitant le processus d'adhésion. L'amélioration de la résistance au perçage des mélanges les rend d'autant plus intéressant pour des applications en emballage flexible.

Comme les mélanges présentaient une morphologie ayant des phases distinctes, nous avons évalué la capacité d'analyser la biodégradation de chaque phase, distinctement, dans un montage de compostage à échelle de laboratoire. Le niveau de dégradation a été suivi à l'aide d'un spectromètre infrarouge à transformée de Fourier muni d'un module de réflexion totale atténuée (FTIR-ATR). Des mélanges binaires de Poly(acide lactique) ou de Polyhydroxybutyrate (PHB) et de Poly(butylène adipate-co-terephthalate) (PBAT) ont été utilisés à cette fin. L'émanation cumulative de CO_2 était mesurée comme indication du niveau de biodégradation de tout l'échantillon. Les résultats de la collecte des gaz ont été analysés avec les résultats obtenus à l'aide du spectromètre FTIR-ATR. Le rapport du pic d'absorption du lien C=O pour le PLA et le PHB vis-à-vis du pic pour le PBAT a diminué graduellement en fonction du temps de

compostage. Ces résultats concordent avec les résultats de la collecte de CO_2 dans le montage de compostage, ce qui démontre la propension de certaines phases des mélanges à se dégrader plus rapidement. Les images prises avec un microscope électronique à balayage (SEM) montrent la formation d'un réseau poreux tridimensionnel (3D) pour les deux types de mélange après 15 jours de compostage. Les résultats de l'accumulation de CO_2 confirment que les mélanges se dégradent à un taux comparable aux résines pures, malgré qu'il soit affecté par le mélange et qu'ils soit inférieur au taux de dégradation des films de PLA et de PHB purs. Nos résultats montrent finalement que les films compostés perdent graduellement leur force de résistance en traction et que le module d'Young des échantillons diminue en fonction du temps de compostage.

ABSTRACT

The urgent necessity of overcoming post-use problems caused by petroleum-based plastic films, which are used in the packaging industry, has provided a great chance to evaluate the potential of bio-based and biodegradable plastics as a viable alternative to petroleum-based polymers. Plastic films in multilayer packages have different functions, such as being barriers to oxygen, water vapor and loss of flavor, and they are required to have certain mechanical, thermal and chemical performances. One function inevitably present in all airtight packages is provided by a layer called the seal layer. This layer guarantees the package hermetic sealing, which assures its barrier performance.

Selection of material for biodegradable seal layers is a huge challenge and is one of the focuses of this thesis. Lack of literature reviews on seal and self-adhesion behavior of biodegradable plastics is one problem. In addition, the available material class of bioplastics is commercially limited, and requires immense preliminary testing of almost every accessible biodegradable resin in order to find suitable plastics for use in seal layer. The seal grade resins were selected over vast initial investigations of more than ten different biodegradable plastics. The property restraints for these resins include their brittleness, low thermal stability, and high crystallinity. Subsequently, film processing and extrusion of these materials require extreme cautions as these biodegradable resins are prone to hydrothermal degradation through melt processing.

Polylactide (PLA) is a commercially available bio-based resin with significant mechanical strength and provides a possibility to tailor the molecular chain in the production line. PLAs, introduced to the market, are divided into two major categories: a crystalline PLA and an amorphous grade. In the course of our initial study the amorphous PLA revealed a better sealing behavior, and therefore, was selected as the main resin in the continuation of our work.

Commercially available bioplastics, cannot fulfill all of the required characteristics of the seal layer for use in packaging applications. Consequently, further modifications are necessary to make them practical for this application. In the specific case of PLA, brittleness is also a great disadvantage. Toughness can be achieved through the melt blending of PLA with other rubbery plastics, e.g. natural rubber, aliphatic polyesters, aromatic copolyesters, polyolefins, etc.

Poly-ε-caprolactone (PCL) and poly (butylene adipate-co-terephthalate) (PBAT) have been selected as representatives of linear aliphatic polyesters and aromatic copolyesters, respectively. These two polymers have been used to modify the mechanical and seal properties of PLA resin.

Simultaneous enhancement of seal properties by using blends of biodegradable resins is another focus of this thesis. Later we will also address the change in the degradability of these resins as a result of blending, in order to find out whether the package can still be regarded as compostable.

Initially in this study, in pursuit of proving the effectiveness of blending to improve the aforementioned properties, blends of Poly (lactic acid) (PLA) and Poly-ε-caprolactone (PCL) were investigated and compared to pure resins in terms of their mechanical and seal performance. All film samples were produced using the cast film process with a thickness of 35 μm. Morphology of the blends was affected by the elongational flow in the film casting die and laminar morphology was developed in blends containing 20wt% and 40wt% PCL. Crystallinity of the blends proved to be affected by low mobility of PLA molecular chains. This provided blends, with more amorphous phase. A noticeable decrease in Seal and Hot-tack initiation temperatures of up to 30°C, as compared to neat PLA, was observed via blending; however, all samples started to seal at temperatures above the melting temperature of PCL of 60ºC. An increase in the Hot-tack strength of the blends, to about 1700g/25.4mm, for a PCL content of 40% showed a significant improvement of self-adhesion in the blend samples. Mechanical properties of the blends were also significantly affected through melt blending. Higher elongation at break and higher toughness were obtained as well, making these blends less prone to defects caused by handling and storage.

PCL as an aliphatic polyester is comparatively costly compared to other polyesters and conventional plastics and has rather low melting and softening points, which results in high production cost as well as handling and storage issues in warm areas. Alternatives to PCL are aromatic copolyesters like PBAT which have higher melting points around 120ºC and lower production costs. The utility of modifying resins with a high melting point requires a deep investigation of crystallinity and its effect on the sealing behavior of these resins.

To provide a deeper understanding of the effect of blending we subsequently used amorphous poly (lactic acid) (PLA) and its blends with Poly (butylene adipate-*co*-terephthalate)

(PBAT). The advantage of this blend, as mentioned above, is that the melting point of PBAT is higher than that of PCL, and hence the blends are thermally more stable. Unlike the PCL case, the melting point of PBAT resin is higher than the sealing temperature of the blends. This will offer the chance to analyze the effect of the change in the crystalline structure of the blends on the shift in its hot-tack initiation temperature. Quenched films of PBAT were used as reference, showing significant shift in its hot-tack initiation temperature (T_{si}) of up to 20°C. Incorporation of PBAT as a dispersed phase lowers the crystal content of PBAT, which also shifts (T_{si}) of the blend samples. The same laminar morphology as the one of the previous blends (PLA/PCL) was obtained. A high aspect ratio of the dispersed phase is important for enhancing the adhesion process. It results in higher surface coverage by a dispersed phase and higher inter-diffusion through sealing. Improved puncture resistance of the blends makes them more interesting for film packaging applications.

As the blends show phase-separated morphology, the last part of this thesis was dedicated to the investigation of the capability of ATR-Fourier Transform infrared techniques to analyze the biodegradation of each phase of samples in a lab-scale composting setup. Two-phase biodegradable blends based on PLA or Polyhydroxybutyrate (PHB), with poly (butylene adipate-co-terephthalate) (PBAT), were used for this part of our work. Cumulatively evolved CO_2 gas was measured as an indication of the extent of biodegradation of whole films in this setup. The results from gas collection have been analyzed together with ATR-FTIR spectroscopy results. The absorption ratio of C=O bond for PLA and PHB to the absorption peak of PBAT decreased gradually as a function of composting time. Latter agrees with evolved CO_2 gas rate in composting setup, showing selectivity of composting to degrade specific phases of the blends. SEM micrographs showed the formation of a porous three dimensional (3D) network for both blends through composting after 15 days. Cumulative CO_2 evolution results confirm that the blends are still degrading by a rate comparative to compostable resins, although this rate is affected by blending and is lower than the degradation rate of pure PLA and PHB films. Our results finally showed that composted films will gradually lose their mechanical strength and the Young's modulus of the samples decreases as a function of composting time.

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LIST OF SYMBOLS AND ABBREVIATIONS

AFM Atomic force microscopy

ASTM American society for testing and material

CAGR Compound annual growth rate

C_g amount of gaseous-carbon produced

C_i amount of carbon in test compound added

DSC Differential scanning calorimetery

E young modulus

E_{pb} puncture energy at break

G' Dynamic storage modulus

G" Dynamic loss Modulus

GPC Gel permeation chromatography

HFFS Horizontal form fill seal

MD Machnine direction

M_n Number average molecular weight

MSW Municipal waste management

OLA Oligomeric lactic acid

OTR Oxygen transmission rate

PBAT Poly(butylene adipate-co-terephthalate)

PCL Poly-ε-caprolactone

PE Polyethylene

PET Polyethylene Terephthalate

PGA Polyglycolide

PHA Polyhydroxyalkanoate

PHB Polyhydroxybutyrate

PLA Poly(lactic acid)

PP Polypropylene

PS Polystyrene

Ps	Seal Pressure
PVOH	Polyvinyl alcohol
SEM	Scanning electron microscopy
T_d	Decomposition temperature
TD	Transverse direction
T_g	Glass transition temperature
TPS	Thermoplastic strach
T_{si}	Self-adhesion initiation temperature
VFFS	Vertical form fill seal
WVTR	Water vapor transmission rate
ΔH_{f100}	heat of fusion of fully crystalline PBAT
ε_b	Elongation at break
ε	Tensile Strain
η^*	Complex viscosity
σ	Tensile Strength

CHAPTER 1 INTRODUCTION

The growing market of flexible packaging and associated increase in plastic consumption requires a deeper understanding of current processes and design of new products for future applications. Packaging applications represent a great portion of plastic market and uses many types of resins and shaping processes. There are both advantages and disadvantages to the use of plastic-based flexible packages and multilayer films in packaging industry. Multilayer film structures will use less amount of polymer per package but at the same time produce polymeric wastes with high aspect ratios, which will result in death of mammals and demise of marine life.(Derraik, 2002; Laist, 1987)

Recycling has been employed to overcome the landfill problems caused by this products but is a limited solution for multilayer packaging. In fact, not all types of plastics are accepted by community recycling programs. Moreover, recycling of multilayer structures needs tedious solvent based techniques that are far from being environmentally friendly.

The new trend is to develop flexible packages based on biodegradable/ compostable materials which will degrade after disposal in soil or in industrial composting facilities and act as nutrients to the soil. These plastics have been developed and enhanced by many companies to be used as substitutes to conventional petroleum-based plastics.

The development of multilayer packages from biodegradable resins requires deep understanding of their basic properties and their behavior in blends with other plastics. Material selection for these packages is limited due to the limited availability and minor production of biodegradable plastics. These plastics still need mechanical, thermal and barrier improvements to become suitable for use in packages. Most of these packages made from biodegradable plastics are aimed for applications where heat sealing is required. Heat sealing protects food and packed materials from ambient oxygen, humidity and microbial contamination while help keep the freshness of the food by preserving its flavor.

The selection of materials for seal applications hasn’t yet been vastly investigated and limitations in the material and process conditions limit the production speed in practical conditions. The seal layer is usually in contact with food and is generally bonded to the barrier layer which requires this layer to seal at preferably low enough temperature not to distort the

properties of the barrier layer. Currently, heat sealing is the most common seal technique in packaging industry and it is preferential to develop biodegradable seal layers which can be sealed using the same instruments with same range of adjustable temperature, pressure and production speed (dwell time) as conventional plastics.

The process parameters can be fixed based on literature review and the effect of resins modification used for seal layer can be followed by series of seal tests performed in simulated conditions. Few peer reviewed studies have been published to address the behavior of biodegradable resins as a seal layer and no detailed analysis of the effect of blending on their seal properties have been yet reported. The development of suitable blends of commercially available biodegradable resins can be the first step in analyzing the behavior of these resins.

Effect of blending on the change in the crystal structure of these resins and its correlation to their seal properties have been seldom studies. Beside the difficulties relative to processing of these materials, they are fairly new to the market and this provides for a limited possibility of choice to develop and analyze seal layers from these polymers.

Research in sealability area of biodegradable resins has been done only by the companies which are introducing these resins. Lack of fundamental and academic studies and reported data on the properties of biodegradable resins and their blends provides limited knowledge of their processing and packaging applications. In addition, there is a chance for blends to have different degradation properties than their pure resins. Investigation of degradability of these resins is mainly focused on their medical applications. Limited published works address the microbial degradation of these materials in composting conditions and few works have addressed their blends composting.

The main objective of this work is to develop compostable blends with comparable seal properties to commercially available olefin-based seal grade products.

To achieve this goal in this thesis, initially we are focusing on clear understanding properties available biodegradable resins and also of blending's effect on improvement of both seal properties and mechanical behavior of them in blends. Blends with several compositions have been prepared and the effect of blend composition on the behavior of their films have been investigated. The blends were made using modifying resins of lower melting point than processing temperature to ensure that the effect of crystallinity and partial melting in the seal process is minimized. Furthermore, to investigate the effect of crystallinity of blends, we used

blends with modifying resins of higher melting point than the sealability temperature window of virgin resin. A fundamental study was performed to develop a correlation between crystal structure of the blends and their self-adhesion initiation temperatures and strength of developed seals from these blends. Finally a combination of composting and ATR-FTIR technique was designed to investigate degradation of separate phases in biodegradable blends in order to be able to investigate the microbial degradation of these blends in simulated industrial composting facilities.

This dissertation is based on three articles that have been accepted or submitted to scientific journals and consists of the following sections:

· Chapter 2 provides a broad literature review considering the related issues and followed by the originality and main objectives of this dissertation.

· The summary and organization of the articles are described in Chapter 3.

· The main achievements of the thesis are given in the format of three scientific papers in Chapters 4, 5 and 6.

· Chapter 7 presents a general discussion of the main results.

· Finally, Chapter 8 presents the final conclusions of this work and the recommendations for future work.

During this project and in collaboration with other members of 3SPack, we had the opportunity to compare the heat seal properties of blends of biodegradable polymers with blends of polyolefin-based copolymers. The results of this sub-project have been published in International Polymer Processing (IPP) (Najarzadeh et al., 2014).

CHAPTER 2 LITERATURE REVIEW

2.1 Plastics in packaging and municipal wastes

Considering the reports on the production of plastics, the global consumption of plastic materials has reached around 250 million metric tons in 2013 with an annual growth of about 3%, as presented in Table 2-1. This amount accounts for a large conversion of crude oil and highlights the importance of foreseeing future alternatives for these polymeric resins (PlasticsEurope, 2014). Packaging makes up for more than one third of the plastic market (39%). A large range of petroleum-based plastics such as polyolefins, polyesters and Nylons as well as polystyrene (PS) have been increasingly used in this industry. These polymers are advantageous due their low cost and high mechanical and barrier properties. Mechanical and barrier properties would guarantee the effectiveness of a package, especially in food packaging applications where the shelf life of products depends significantly on the Oxygen Transmission Rate (OTR), Water Vapor Transmission Rate (WVTR) and the rate at which the flavor is lost from the package. (Bucci et al., 2005; Sadeghi et al., 2013; Sinclair, 1996; Wagner, 2009)

*Table 2-1*Global consumption of biodegradable polymers, 2000, 2005 and 2010(Platt & Limited, 2006)

Global consumption of biodegradable polymers, 2000, 2005 and 2010 (‘000 tonnes)				
	2000	2005	2010*	%CAGR 2005-2010
Western Europe	15.5	55.7	129.4	18.4
North America	6.7	21.3	46.5	16.9
Asia Pacific	5.8	17.8	38.5	16.7
Total	28.0	94.8	214.4	17.7

* Prediction based on annual growth rate

Recent concerns about the biological and environmental dangers of plastics in landfills and the fact that these materials are not totally recyclable and/ or compostable favors the replacement of these resins with biodegradable counterparts.(Bucci et al., 2005; Garlotta, 2001; Lucas et al., 2008; Reddy et al., 2003; Shah et al., 2008; Sinclair, 1996) Municipal Solid Wastes (MSW) represent a growing problem, which is mainly due to the limitations in landfilling plastic materials. Recent awareness of environmental hazards evoked by plastics imposes to packaging industry the use of more environmentally friendly features in packaging. (Kirwan & Strawbridge, 2003; Najarzadeh et al., 2014; Sinclair, 1996)

2.1.1 Biodegradable and compostable plastics

To make an acceptable definition of biodegradable polymers and bio-based polymers there are certain standards that can be followed, and organizations such as the European Bioplastics and Bioplastic Council have put certain limitation to what can be called biopolymer or bio-based plastics. According to the American Society for Testing and Materials (ASTM) the term compostable cannot be used interchangeably to the term biodegradable. "*Compostable plastic is* a plastic that undergoes degradation by biological processes during composting to yield CO_2, water, inorganic compounds, and biomass at a rate consistent with other known compostable materials and leave no visible, distinguishable or toxic residue" while "*biodegradable plastic is* a degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae."(ASTM D6400 2012; ASTM D5338 2011). Regardless of the source of plastics, it is the chemical structure of a polymer molecular chain that determines its biodegradability. (Shah et al., 2008) In other words, there are many bio-based polymers such as Nylon 11 and Nylon 9, which are not biodegradable and many petroleum-based polymers such as Poly-ε-caprolactone (PCL) or Poly(butylene adipate-co-terephthalate) (PBAT) which are biodegradable.(Garlotta, 2001; Grima et al., 2000; Lucas et al., 2008; Sarazin et al., 2004; Shah et al., 2008)

2.1.2 Classification of biodegradable plastic

Vast categories of biodegradable polymers have been synthesized and developed. They have been used in various applications as is or have been modified to enhance their processability or other properties, to make them suitable for specific needs. All these polymers have certain molecular structures to provide them with biodegradability. Here we categorize these polymers based on both their sources of production and their chemical structures.

a Biopolymers products from agricultural resources

These polymers consist of two main categories including polysaccharide derivatives and Proteins and lipids derivatives:

I Polysaccharides:

Polysaccharides are starches from wheat, potato, maize and similar bio-resources and cellulose-based products from wood, straws and related resources. Other polymers in this category are pectins, lignin, chitosan and chitin.

Starch in its natural form is not processable and needs chemo-mechanical modification. (Li et al., 2011; Park et al., 2000; Rodriguez-Gonzalez et al., 2004). Once prepared, Thermoplastic Starch (TPS) shows interesting features such as compostability and low cost. The processability of TPS is acceptable and it can be normally processed with routine machines used for processing thermoplastics. Depending on type and amount of plasticizer, the mechanical properties can be adjusted in a wide operation window. (Avérous, 2004; Li et al., 2011)

Low clarity, moisture sensitivity and considerably low mechanical properties compared to other biodegradable plastics are among the disadvantages limiting the use of TPS in packaging, particularly for food packaging applications. (Avérous, 2004)

II Proteins and Lipids

This category usually consists of proteins from dairy products like casein, Whey and also Gelatin and Collagen that are from animal sources and zein, soya and gluten, which are plant-based. (Kim & Ustunol, 2001)

b Biopolymers from micro-organisms

This category makes for a large number of plastics used in packaging industry, adding up for almost ten percent of bioplastics market (Barker et al., 2009), which are making the Poly(hydroxy alkanoates) family (PHAs). PHB as the main member of this group has been at the center of notice to be replacing other biodegradable polymers like PLA in packaging application, but as will be explained the intrinsically failure in crystal structure of this material has still forced it out of the main market competition Main products in this category are:

1 Poly(hydoxy butyrate) (PHB)

PHB is the main polymer in the family of Poly (hydroxyl alkanoates). A deep understanding of its synthesis and chemical characteristics is given in the works of Reddy et al.

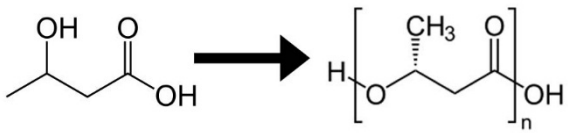


Figure 2.1-1. Chemical structure: left 3-Hydroxybutyric acid; right Poly (hydroxy butyrate) (PHB) (Reddy et al., 2003)

PHB is known for its good hydrolysis resistance, mechanical strength and barrier strength. (Reddy et al., 2003) This polymer has been used in many different applications and has been looked through for packaging applications too. (Bucci et al., 2005)

PHB belongs to the polyester class of polymers and has been produced by different type of bacteria, under optimal culture conditions. Chemical structure of this resin is given in Figure 2.1-1.(Reddy et al., 2003) Main microorganisms producing this polymer are genera Alcaligenes, Azobacter, Bacillus and Pseudomonas (Bucci et al., 2005; Manna & Paul, 2000; Reddy et al., 2003). Combination of PHB's properties such as high stability at ambient temperature, high modulus of elasticity, high resistance to hydrolysis, with its high rate of degradation in microbial environment is making PHB a potential polymer to replace polyolefins in many application such as packaging. (Bucci et al., 2005) Along with the properties and synthesis of PLA and PCL resins given in Table 2-2 and *Table 2-3* for the sake of comparison different grades of PHB produced at present and commercially available in the market, are also given in *Table 2-4*. The effects of aging and crystallinity on the mechanical properties of PHB resin were investigated by many researchers (Barham & Keller, 1986; Corre et al., 2012; Kaplan, 1998). Bruzaud et al. and Demarquette et al. showed that the inter-lamellar secondary crystallization accounts for increasing the modulus of elasticity and brittleness of PHB samples. Addition of plasticizers can in some cases worsen the problem by increasing the rate of secondary crystallization due to higher chain mobility of plasticized samples.(Barham & Keller, 1986; Corre et al., 2012)

Barham and keller showed that the intrinsically occurring radial and circumferential cracks in crystallized PHBs, is the main reason for its mechanical failure. These cracks develop due to development of high stress between highly crystalline and amorphous phases of PHB resin that are shown in Figure 2.1-2

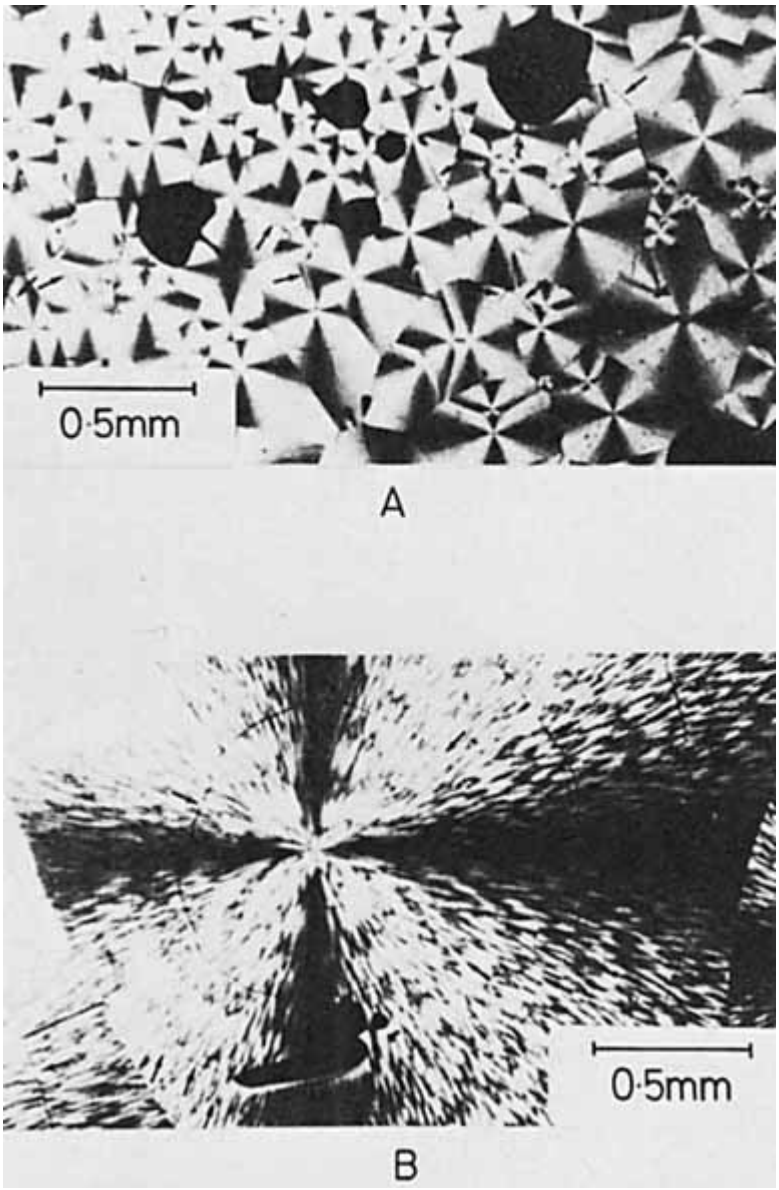


Figure 2.1-2. Optical micrographs taken between crossed polars of an unstrained thin films of PHB (a) crystallized at 60°C, (b) crystallized at 130°C. The radial cracks in (a) and circumferential cracks in (b) are indicated by arrows. (Barham & Keller, 1986)

These failures are shown to be resolved using different techniques which all tend to lower the secondary crystallization and hence improve the elongation at break and mechanical properties of PHB. (Barham & Keller, 1986; Corre et al., 2012; Kaplan, 1998) although in the case of flexible packaging and film processing there are still unresolved weaknesses and disadvantages to be fixed.

2 Poly (hyroxybutyrate-co-hydroxyvalerate)

A step forward to overcome the mechanical shortages of PHB resin is to use a co-monomer in its synthesis process. (Reddy et al., 2003) This would result in a polyester with reduced crystalline phase and, depending on the content of valerate co-monomer, higher flexibility. This process is used in the production of many articles especially medical devices. (Holland et al., 1987; Yasin & Tighe, 1992) Recently, this copolymer has found its path to packaging applications although it is less advantageous than PHB in terms of oxygen and water vapor transmission rates. (Ketonen, 2011; Priyanka & Nandan, 2014)

c Polymers synthesized from monomers derived from natural resources

1 Polylactide (PLA)

This polymer is classified as aliphatic polyester. Aliphatic polyesters are making one of the main classes of biodegradable polymers used in packaging applications. (Sinclair, 1996; Wagner, 2009) This category of materials is mostly made from α-hydroxy-acids. (Garlotta, 2001) PLA is widely used in many applications ranging from food packaging to medical devices. (Grizzi et al., 1995; Li et al., 2011; Najarzadeh et al., 2014; Sarazin et al., 2004; Sinclair, 1996) PLA can be produced also from 2-hydroxy propionic acid (Lactic acid). This monomer can have two stereospecific enantiomers called L-lactic(+) acid and D- Lactic acid(-) presented in Figure 2.1-3, thus PLA's tacticity and streospecificity can be designed by different chain sequencing given in *Table 2-5* yielding different thermo-mechanical properties. (Kaihara et al., 2007)

PLA is well known for its comparatively high modulus of elasticity and transparency. Due to its high clarity and brittleness, some comparison of its basic properties with those of polystyrene have been made in the work of Sinclair et al. as illustrated in Table 2-2 (Garlotta, 2001; Grizzi et al., 1995; Najarzadeh et al., 2014; Sinclair, 1996).

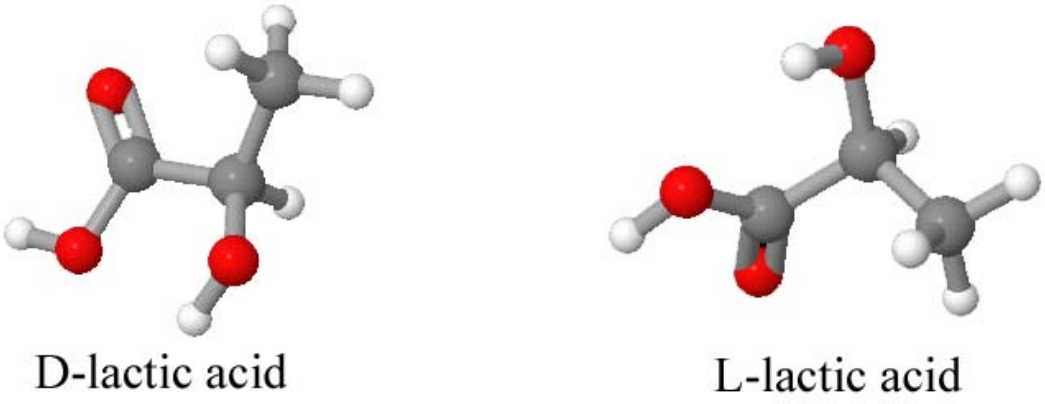


Figure 2.1-3 L-lactic acid and D-lactic acid enantiomers
(http://www.chemeddl.org/resources/models360/models.php?pubchem=107689)

In industrial synthesis production of this material by ring opening polymerization of lactide form, is more common which is illustrated in Figure 2.1-4 (Garlotta, 2001; Grizzi et al., 1995; Hartmann, 1998; Kaihara et al., 2007; Sinclair, 1996; Wehrenberg, 1981)

Table 2-2 Some basic properties comparison of Poly (lactic acid) and Polystyrene(Sinclair, 1996)

	PLA[a]		PS[b]	
Physical property	Oriented	Unoriented	Oriented	Unoriented
Ultimate tensile strength:[c]				
psi	14,700	6,900	7,400	7,015
MPa	101	48	51	48
Elastic modulus:				
psi	564,000	221,000	450,000	240,000
MPa	3,889	1,524	3,103	1,655
Elongation, %	15.4	5.8	4.0	–
Impact strength, notched Izod:				
ft-lb/in	–	0.44	0.4	0.24
mN/m	–	23	21	13
Deflection temperature under load:				
°F	181	127	200	–
°C	83[d]	53	93[e]	–
Specific gravity	1.25	1.25	1.05	1.05
Melt flow rate:				
200°C	–	46	–	3.5
155°C	–	2	–	–

[a]L-/D,L-Lactide copolymer.
[b]Crystal polystyrene, Amoco R3.
[c]ASTM D882.
[d]Annealing temperature.
[e]264 psi (1.82 MPa).

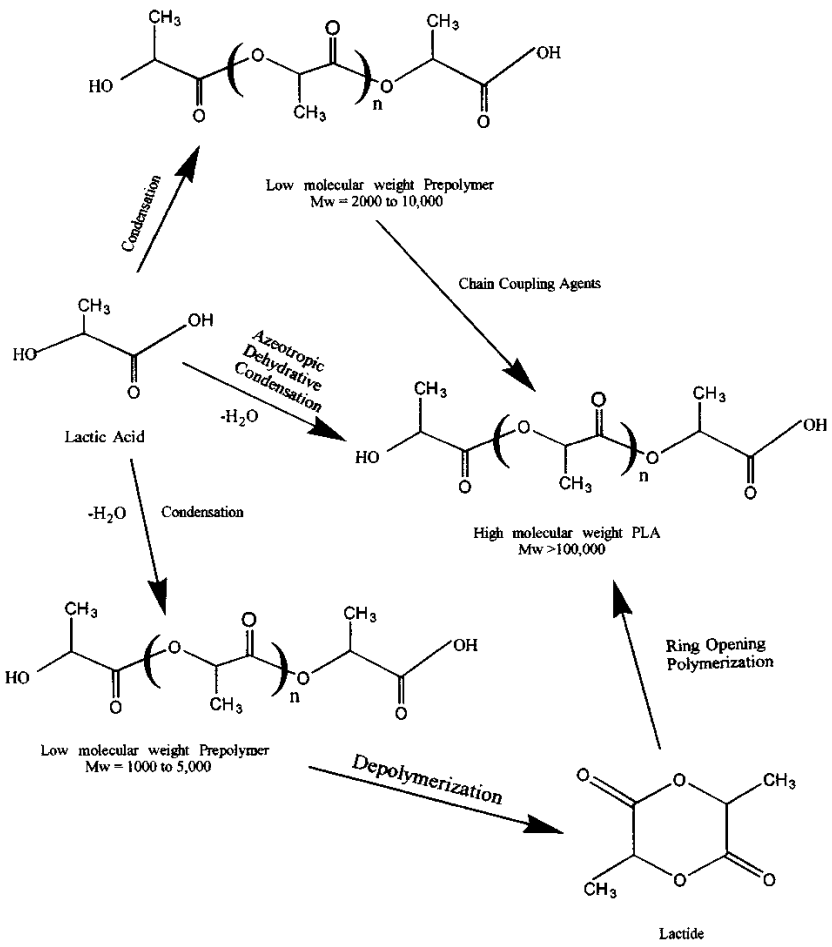


Figure 2.1-4. Synthesis methods for high-molecular-weight PLA (Garlotta, 2001; Hartmann, 1998; Lunt, 1998)

Many researchers have long investigated mechanical brittleness of PLA, and different grades of plasticizers and modifying resins have been used to resolve this issue. Copolymerization can also give promising results to modify and improve the rigid molecular chains of PLA and hence allow producing articles of higher toughness. (Anderson et al., 2008; Liu et al., 2010; Oyama, 2009; Sinclair, 1996; Takayama et al., 2006; Theryo et al., 2010; Theryo et al., 2011) The residue of lactic acid, lactides and oligomeric lactic acids (OLA) from PLA polymerization were shown to have plasticizing effects (Braun et al., 2006; Sinclair, 1996). These residues are often undesirable in many applications such as medical devices and food packaging due to the migration phenomena and odor production (Braun et al., 2006; Garlotta, 2001). Braun et al. have shown that determination of the amount of this inevitable residue can be made possible through a novel infrared assisted technique, which will be explained, in the next section, where we also made use of to develop our detection procedure together with the composting setup. (Braun et al., 2006)

On the processing point of view, stability of PLA in process is of great importance. The rheological studies, monitoring of mechanical properties before and after processing and examination of change in molecular weight of PLA have demonstrated the tendency of this polymer to degrade after processing and revealed its low thermal stability (Auras et al., 2004; Gupta & Deshmukh, 1982; Jamshidi et al., 1988; Najafi et al., 2012b; Signori et al., 2009; Södergård & Näsman, 1994)

Addition of plasticizers and melt blending with modifying resins can help lower the processing temperature and prevent aggressive degradation, while addition of chain extenders was shown to recombine the broken chains of PLA and even increase its molecular weight as depicted in Figure 2.1-5 (Najafi et al., 2012a; Signori et al., 2009; Södergård & Näsman, 1994). Loss of clarity and a decrease in elastic modulus as well as tensile strength are however disadvantages of this method.

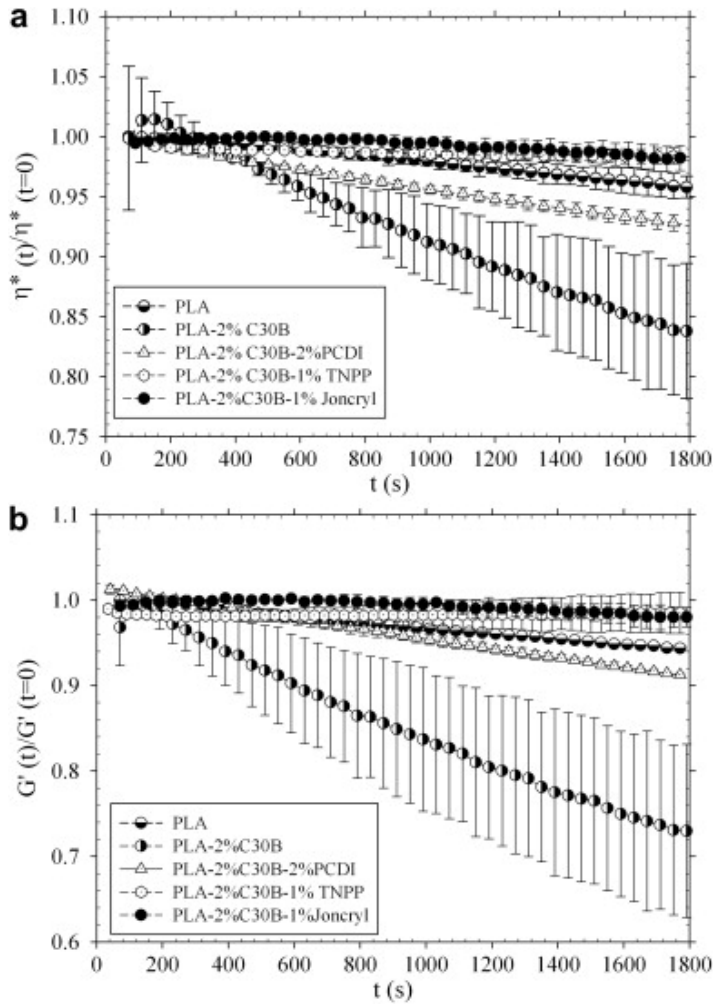


Figure 2.1-5 Normalized complex viscosity (a) and storage modulus (b) of neat PLA and PLA nanocomposites with and without chain extender as a function of time at ω=6.28 rad/s and T= 190 ºC.

d Biodegradable plastics synthesized from petroleum based monomers

Polymers synthesized from petroleum based sources include a great number of aliphatic and aromatic polyesters, co-polyesters and poly ether amides.

I Poly-ε-caprolactone (PCL)

PCL is an aliphatic polyester which is synthesized from ring opening reaction of caprolactone as shown in Figure 2.1-6

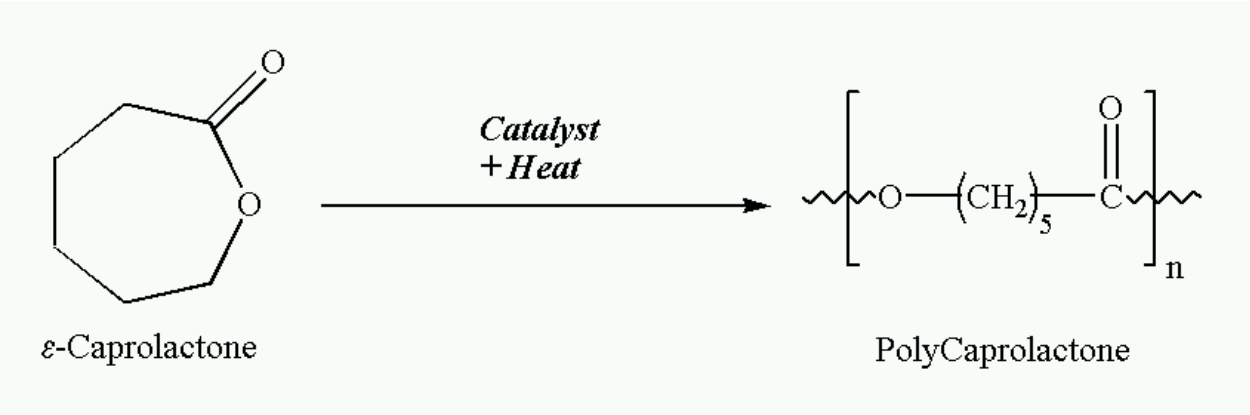


Figure 2.1-6 Ring opening polymerization of ε-caprolactone to poly-ε-caprolactone

A completely linear structure of poly-ε-caprolactone gives PCL some similar properties to polyethylene (PE) while the ester bond makes it biodegradable and prone to in-vitro and in-vivo hydrolysis. Some properties of PCL are summarized in Table 2-3.

Table 2-3 Properties of PCL (Labet & Thielemans, 2009)

Properties	**Range**	**Ref**
Number average molecular weight ($M_n(g.mol^{-1})$)	530–630 000	___
Density($g.cm^{-3}$)	1.071–1.200	(Gross & Kalra, 2002; Iroh, 1999; Van de Velde & Kiekens, 2002)
Glass transition temperature($T_g(°C)$)	(−65)–(−60)	(http://www.absorbables.com/; Ikada & Tsuji, 2000; Sinha et al., 2004; Van de Velde & Kiekens, 2002)
Melting temperature ($T_m(°C)$)	56–65	(Ikada & Tsuji, 2000; Van de Velde & Kiekens, 2002)
Decomposition temperature ($T_d(°C)$)	350	(http://www.absorbables.com/; Lam et al., 2007)
Tensile Strength (σ (MPa))	4–785	(Gross & Kalra, 2002; http://www.absorbables.com/; Ikada & Tsuji, 2000; Van de Velde & Kiekens, 2002)
Young modulus (E (MPa))	0.21–0.44	(Van de Velde & Kiekens, 2002)
Elongation at break (ε_b (%))	20–1000	(Gross & Kalra, 2002; Iroh, 1999; Van de Velde & Kiekens, 2002)

PCL has comparatively low glass transition temperature (T_g) and low Young modulus and the commercial grades have a high elongation at break, which makes it very interesting as a modifier to enhance mechanical properties of other brittle polyesters in this material class (i.e.

PLA and PHB). (Anderson et al., 2008; Takayama et al., 2006) Nevertheless, low melting point of PCL and its cost have been drawbacks to its wide applications in packaging industry.

II Poly (butylene adipate-co-terephthalate) (PBAT)

PBAT is an aromatic co-polyester with a wider range of properties than PCL as this polymer can be tailored by changing the sequences of the block copolymer. Alvarez et al indicated using a similar process in a related co-polyester of this family, Poly (butylene isophthalate-co-butylene adipate), a broad range of properties obtained can be achieved. (Alvarez et al., 2003) Chemical structure of PBAT is illustrated in Figure 2.1-7.

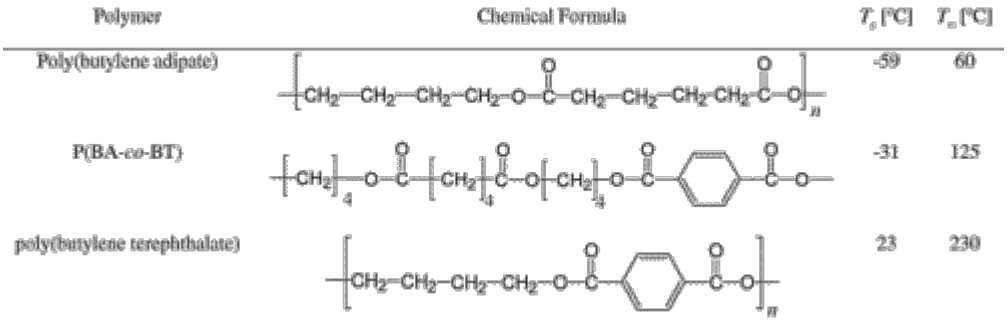


Figure 2.1-7 chemical structure of PBAT co-polyester and homopolymers of Poly(butylene terephthalate) and poly(butylene adipate) (Cranston et al., 2003)

Due to high compatibility of PBAT with PLA, this polymer has attracted many attentions and have been used to improve the mechanical properties and toughness of PLA samples. (Jiang et al., 2009; Jiang et al., 2005; Kumar et al., 2010; Lee et al., 2007; Signori et al., 2009; Weng et al., 2013; Xiao et al., 2009; Zhang et al., 2009) Amount and type of crystals significantly change the properties of PBAT. A detailed analysis of its crystalline structure was reported by Kuwabara et al. and in a work of Cranston et al. (Cranston et al., 2003; Kuwabara et al., 2002). Poly(butylene adipate-co-terephthalate) has higher melting point than PCL, which gives it higher thermal stability and its higher T_g results in a wider application temperature window.

In packaging applications, blends of PLA and PBAT have been suggested and used as compostable shopping bags and many research works have been done to optimize the film development processes. (Sirisinha & Somboon, 2012).

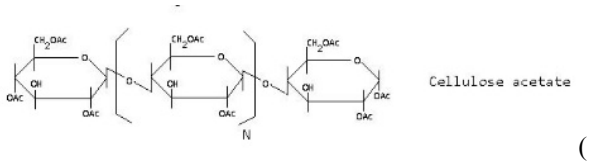
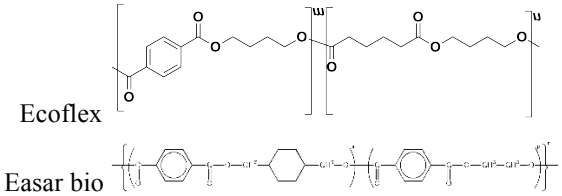
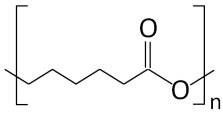
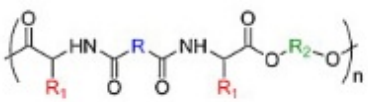
2.1.3 Classification of biodegradable plastics based on their chemical class and their producers

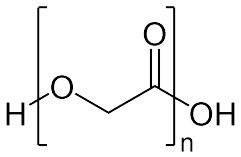
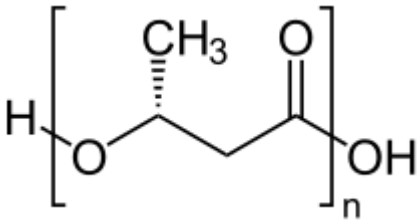
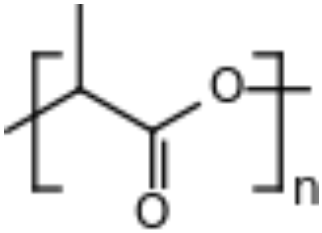
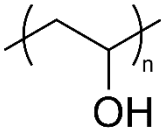
The degradability of plastics is completely dependent on their chemical structures and no matter if they are sourced from natural raw material or from petroleum-based monomers the

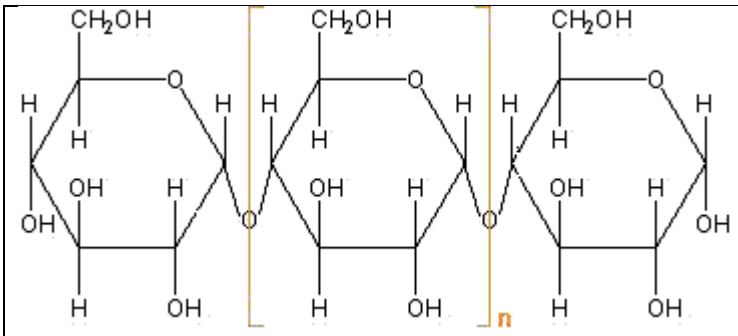
biodegradability depends totally on the structure of the molecular chain. Beside the chemical structure a look at the market for material selection is essential. Larger companies tend to provide more general purpose grades of polymers with lower future cost targets, where smaller companies tend to produce more of a specified tailored medical and military targeted products which are not seem to be cheaper in close future.

We provide in this section a brief list of biodegradable polymers providing their chemistry and manufacturing companies. An overview of their structure and producers is given by Averous as presented in Table 2-4(Avérous, 2004)

Table 2-4. Classification of biodegradable polymers on the basis of material class

biodegradable polymers		
Material class	Manufacturer	Product name
Cellulose acetate  (polysaccharide)	Mazzucchelli	BIOCETA®
	Planet Polymer	EnviroPlastic®-Z
Copolyester  Ecoflex Easar bio	BASF	Ecoflex
	Eastman	Easter Bio™
Polycaprolactone (PCL)  (Aliphatic polyester)	Birmingham Polymers	Poly(ε-caprolactone)
	Planet Polymer	Enviroplastic®-C
	Solvay	CAPA®
	Union Carbide	TONE®
Poly(ester amide) 	Bayer	BAK 1095
		BAK 2195

Poly(ethylene terepthalate) (PET)- modified	DuPont	Biomax®
Polyglycolide (PGA) 	Alkermes	Medisorb®
	Birmingham Polymers	Poly(glycolide)
	Boehringer Ingelheim	Resomer®
	PURAC	PURASORB® PG
Polyhydroxyalkanoates (PHA) 	Metabolix	PHA
	Biomer	Biomer™
	Monsanto	Biopol®
Poly(lactic acid) (PLA)  (Aliphatic Polyester)	Alkemers	Medisorb®
	Birmingham Polymers	Poly(L-lactide) & Poly(DL-lactide)
	Boehringer Ingelheim	Resomer®
	Cargill Dow Polymers	Natureworks®
	Chronopol	Heplon™
	Hygail	PLA
	Neste	Poly(L-lactide)
	PURAC	PURASORB® PL/PD/PDL
Poly(vinyl alcohol) (PVOH) 	Idroplast	Hydrolene®
	Kurary	Mowiflex TC®
	Novon	Aqua-NOVON®
	Planet Polymer	Aquadro™
	Texas Polymer	Vinex™
Starch & starch blends	AVEBE	Paragon™
	BioPlastic (Michigan)	Envar™
	BIOTEC	Bioplast®, Bioflex®, Biopur®

	Buna Sow Leuna	Sconacell®
	Cerestech	Thermoplastic starch blends
	Midwest Grain	Polytriticum™ 2000
	Novamont	Mater-Bi™
	Novon	Poly-NOVON®
	Starch Tech	ST1, ST2, ST3
Other blends	Alkermers	Medisorb®
	Bio Plastic (Colorado)	Biocomposite material
	Birmingham Polymers	Poly(DL-lactide-co-caprolactone)& & Poly(DL-lactide-co-glycolide)
	Boehringer	Resomer®
	Planet Polymer	EnviroPlastic®-U
	PURAC	PURASORB® PLG,
		PURASORB® PDLG

The distinctive difference between biodegradable and conventional plastics lays in their capability to be degraded after use. Hence practically they should have no shortage in the mechanical, barrier and processability during their useful life. (Bucci et al., 2005; Cha & Chinnan, 2004; Kirwan & Strawbridge, 2003; Sinclair, 1996) However, state of art technologies do not provide with biodegradable plastics as superior as conventional petroleum based resins and the modification of their mechanical, barrier and seal behavior is still inevitable. (Anderson et al., 2008; Hashima et al., 2010; Liu et al., 2010; Najarzadeh & Ajji, 2014b; Oyama, 2009; Taib et al., 2012; Takayama et al., 2006; Theryo et al., 2010; Ying-Chen et al., 2010)

2.1.4 Processing and properties of biodegradable plastics for packaging applications

Beside Starch based biodegradable resins, which are not at the focus of our study, PLA constitutes the largest portion of biodegradable polymers used in the food packaging market. PLA has significant advantages, which attracts many researchers to modify it for different applications. (Garlotta, 2001; Najarzadeh & Ajji, 2014b; Nampoothiri et al., 2010; Sinclair,

1996) Clarity, High tensile strength and high young modulus together with its good processability give it a chance to be a potential replacement for conventional petroleum based plastics.

a Toughening and mechanical property improvement

Trends to modify and improve the mechanical properties of PLA have been at the center of attention of research works. (Anderson et al., 2008) Molecular weight and crystallinity affect the mechanical properties of Polylactides. Perego et al. have shown that the Homopolymer of L-lactide has superior properties than copolymer of D,L Lactides. Higher thermal deflection temperature, higher tensile strength and modulus and also better effect of annealing on these properties are some advantages of this homopolymer. (Perego et al., 1996)

Combination of enantiomers of lactic acid either as co-monomers or stereocomplex mixture have been used and analyzed by many researchers.

Table 2-5. Melting Point and Glass Transition Data for PLA Structure and Blends

PLA Structure	Description	T_m (°C)	$T°_m$ (°C)	T_g (°C)
Isotactic poly(L-lactide) or poly (D-lactide)	LLLLLLLLL or DDDDDDDDDD	170-190	205 211 215	55-65
Random optical copolymers	Random level of meso or D-lactide in L-lactide or D-lactic acid in L-lactic acid	130-170	165-210	45-65
PLLA/PDLA stereocomplex	LLLLLLL mixed with DDDDDDDD	220-230	279	65-72
PLLA/PDLA stereoblock complexes	LLLLLLLLLLDDD DDDDD	205 179		
Syndiotactic poly(*meso*-)PLA	DLDLDLDLDLDL Al-centered R-Chiral catalyst	152		40
Heterotactic	LLDDLLDDLLDDLL			40

(disyndiotactic) poly(*meso*-lactide)	DD Al-centered *rac*-Chiral catalyst			
Atactice poly(*meso*-lactide)	No stereocontrol			46
Atactic PDLLA	No stereocontrol			53

The results of change in the melting point and glass transition temperature measurements of pure, blends and copolymer of polylactides are presented in Table 2-5. The copolymers as shown in this table have lower melting points than pure PLLA or PDLA and introduction of each of the monomers to the copolymer for about 10% results in amorphous copolymers. Stereocomplex blends are blends of PLLA and PDLA at 50% concentration of each, which result in a synergistic effect on the crystals formed in their blends, resulting in an increase of the melting point to about 230ºC (Henton et al., 2005).

Blending has seen its potential in increasing the toughness of PLA. Many researchers suggested many other techniques such as plasticization and copolymerization and in cases use of a chain extender. (Anderson et al., 2008; Hashima et al., 2010; Liu et al., 2010; Najafi et al., 2012a; Oyama, 2009; Taib et al., 2012; Takayama et al., 2006; Theryo et al., 2010; Theryo et al., 2011)

The American Society for Testing and Materials (ASTM) provides two methods for the assessment of toughness of polymers and their blends as well as their composites. These two methods are impact testing and tensile testing. Both of the tests can be used to measure the change in the toughness of a material based on the modification of a particular property. Nevertheless, none of the tests give detailed knowledge of the highest possible toughness state reached by said modification. In other words, a material which presents a high impact strength may show insignificant improvement in elongation at break. (Anderson et al., 2008) For applications where high deformation is applied to the material, the measurement of tensile toughness seems to be more promising.

A detailed analysis of biodegradable polymers used for toughening of PLA can be found in the work of Anderson et al. where they have analyzed the effect of improving the toughness of

PLA on the total mechanical behavior of this resin. (Anderson et al., 2008) Poly-ε-caprolactone (PCL) and Poly (butylene adipate-co-terephthalate) (PBAT), as illustrated in Figure 2.1-8, are among the biodegradable resins which display promising results in improving the tensile toughness of PLA. (Anderson et al., 2008; Hiljanen-Vainio et al., 1996; Jiang et al., 2005; Maglio et al., 1999; Najarzadeh et al., 2014; Sirisinha & Somboon, 2012)

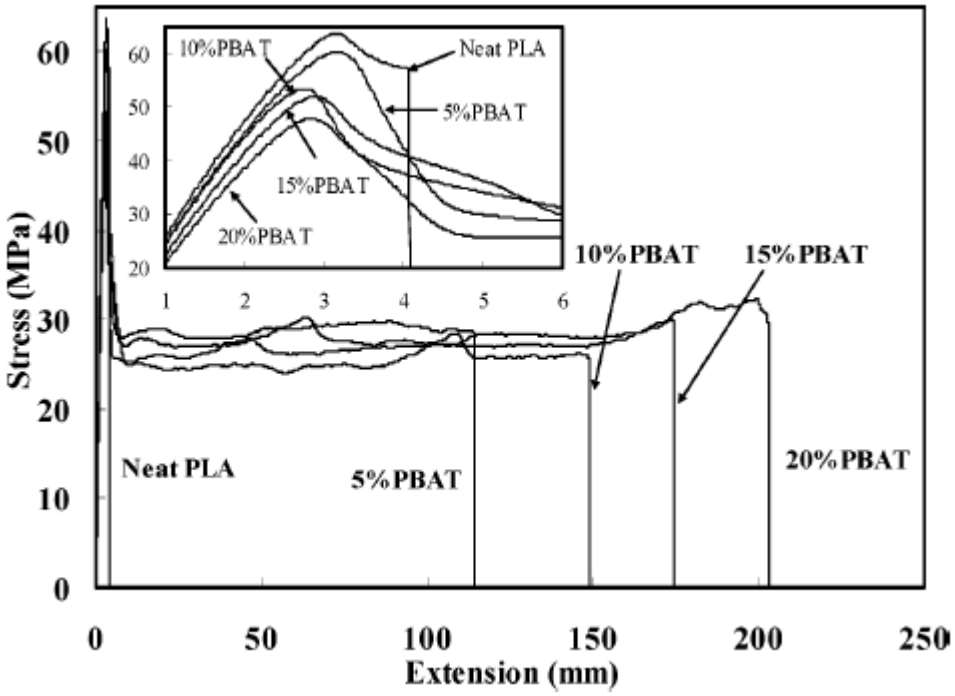


Figure 2.1-8 Tensile stress−extension curves of the blends with different PBAT contents. The inset gives details of stress−extension of the blends in the neighborhood of yield points.(Jiang et al., 2005)

b Melt rheology of PLA and its blends

Approach to the blending of biodegradable polymers likewise other polymeric systems requires the understanding of melt behavior of these resins. Rheological data have been collected and analyzed by many researchers and have been interpreted considering the molecular weight, stereochemistry and composition of the blends. Main difficulties were associated with uncertainty in the measurement of molecular weights and assessment of melt stability. This results in inconsistency in the reported behavior of different PLA samples.

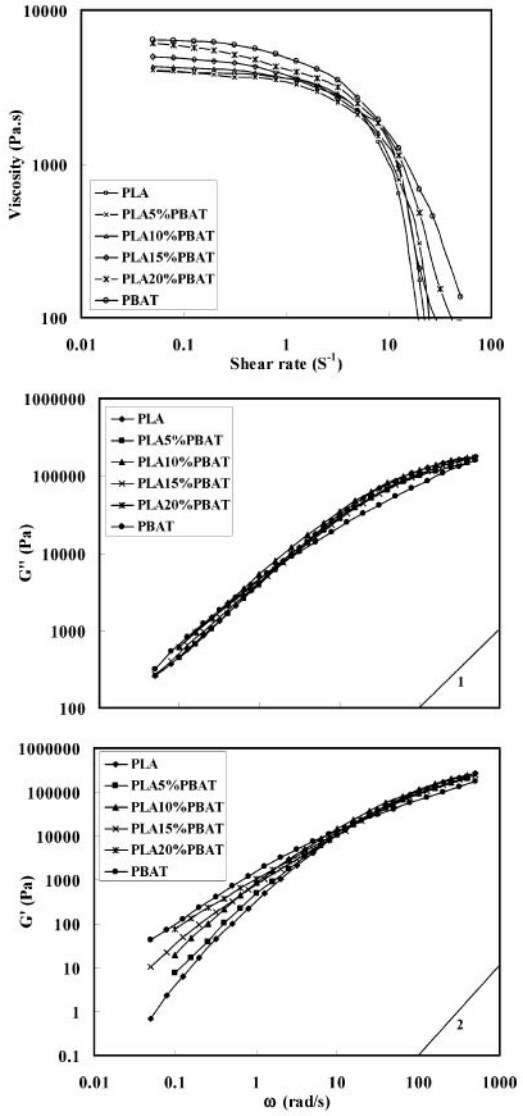


Figure 2.1-9 Steady shear viscosity, loss modulus(G") and storage modulus(G') of PLA and its blend with PBAT (Jiang et al., 2005)

The viscoelastic behavior of blends of PLA/PCL has been studied by many researchers. There is a general agreement on the development of co-continuous morphology at concentrations between 40-60 wt% PCL in the blends. (Sarazin et al., 2004; Wu et al., 2008) A shift in the rheological behavior is expected by the phase inversion happening at those concentrations. PCL dispersed phase tends to form larger domains in PLA as the PLA/ PCL viscosity ratio forces the droplets of PLA to break faster during the melt blending process where the PCL is the continuous phase.

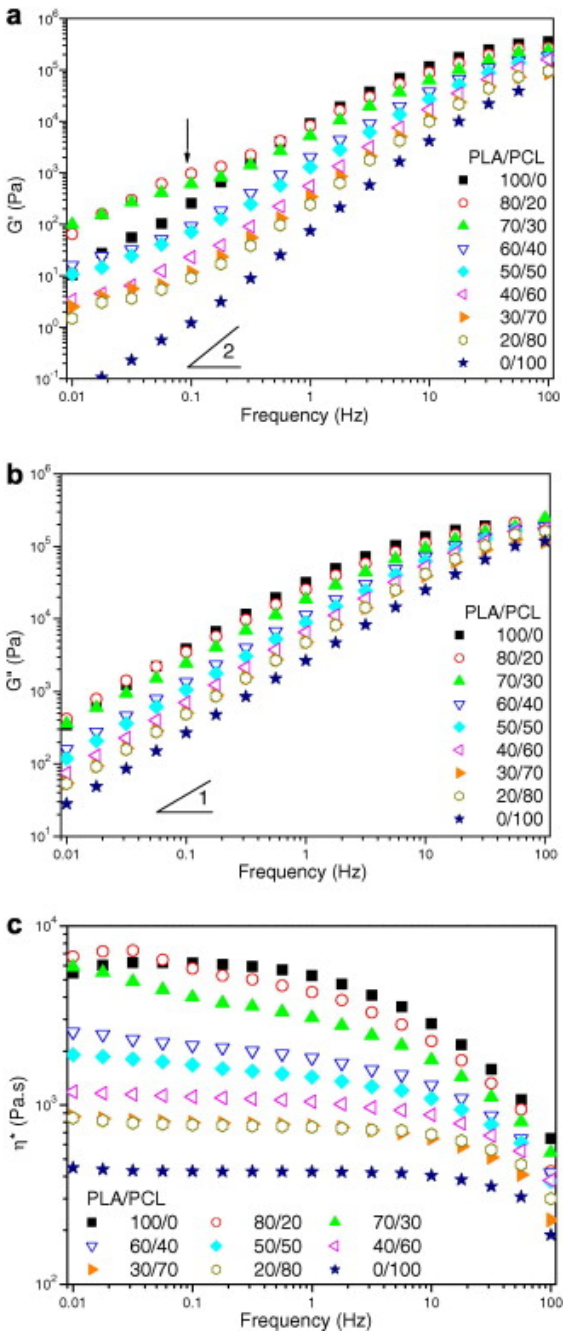


Figure 2.1-10 (a) Dynamic storage modulus (G'), (b) dynamic loss modulus (G") and (c) complex viscosity (η) for the PLA/PCL blend obtained in dynamic frequency sweep.(Wu et al., 2008)*

Thermal instability as has been mentioned before, is the main difficulty in measurement of viscoelastic properties of PLA, but is less pronounced in blends with PCL and PBAT Figure 2.1-9 and Figure 2.1-10. Effect of chain extender on the rheological behavior of PLA and its composites have been investigated by Najafi et al.(Najafi et al., 2012b) Suitable chain extender

can result in increasing the viscosity of PLA as a result of intermolecular crosslinking, which results in higher number of long chain branching.

c Morphology study of Biodegradable blends

The study of the properties of polymeric blends is inseparable of its morphology and understanding of the miscibility and shape of phases in binary, and multiphase blends. (Ajji & Utracki, 1996; Avgeropoulos et al., 1976; Paul, 2012; Scott & Macosko, 1995; Sundararaj & Macosko, 1995; Utracki & Favis, 1989; Utracki & Shi, 1992; Wu, 1990) Combination of viscosity ratio, interfacial tension and field of stress as well as blend's composition during processing of the blends results in different morphologies. In polymers with similar chemical structures, such as polyesters, viscosity ratio plays a significant role in the control of morphology. (Gonzalez-Nunez et al., 1993; Sarazin et al., 2004) Blends of PLA/ PCL and PLA/PBAT have been of interest of researchers. Detailed morphological studies have been carried out to find the affecting parameters on the development of various types of morphology. (Cabedo et al., 2006; Jiang et al., 2005; Kumar et al., 2010; Sarazin et al., 2004; Takayama et al., 2006; Weng et al., 2013; Wu et al., 2008)

Matrix dispersed morphology have been reported for both PLA/PCL and PLA/PBAT in the range of 5 to 40 wt. % dispersed phase. (Nampoothiri et al., 2010; Sarazin et al., 2004; Wu et al., 2008) Wu et al. have suggested the gradual changes in the morphology of PLA/ PCL blends depending on their composition, Figure 2.1-11

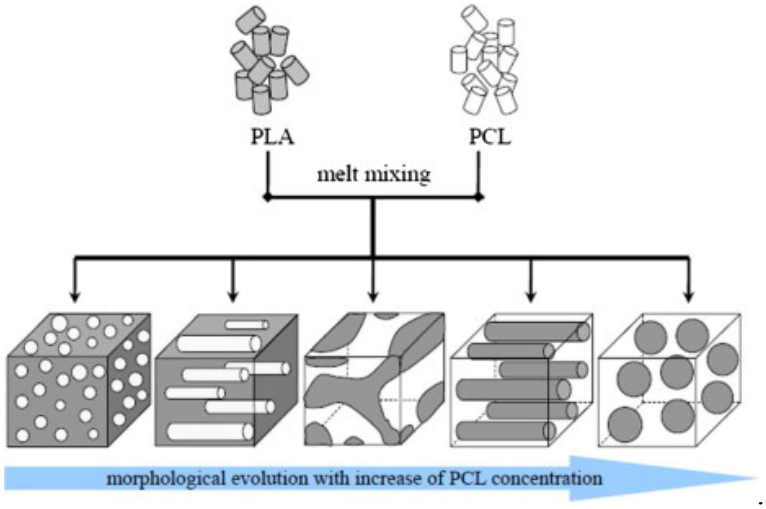


Figure 2.1-11 Schematic diagrams of the morphological evolution for the PLA/PCL blend with increasing PCL concentrations. The white part is PCL phase and the gray part is PLA phase.(Wu et al., 2008)

Investigations of the morphology of the blends and the detection of phase separation have been performed using several techniques. Microscopy techniques are the most common tools for morphological studies, among which the Scanning Electron Microscopy (SEM), as illustrated in Figure 2.1-12 and Figure 2.1-13, was utilized widely by many researchers. Atomic Force Microscopy (AFM), Figure 2.1-13, have also been commonly used.

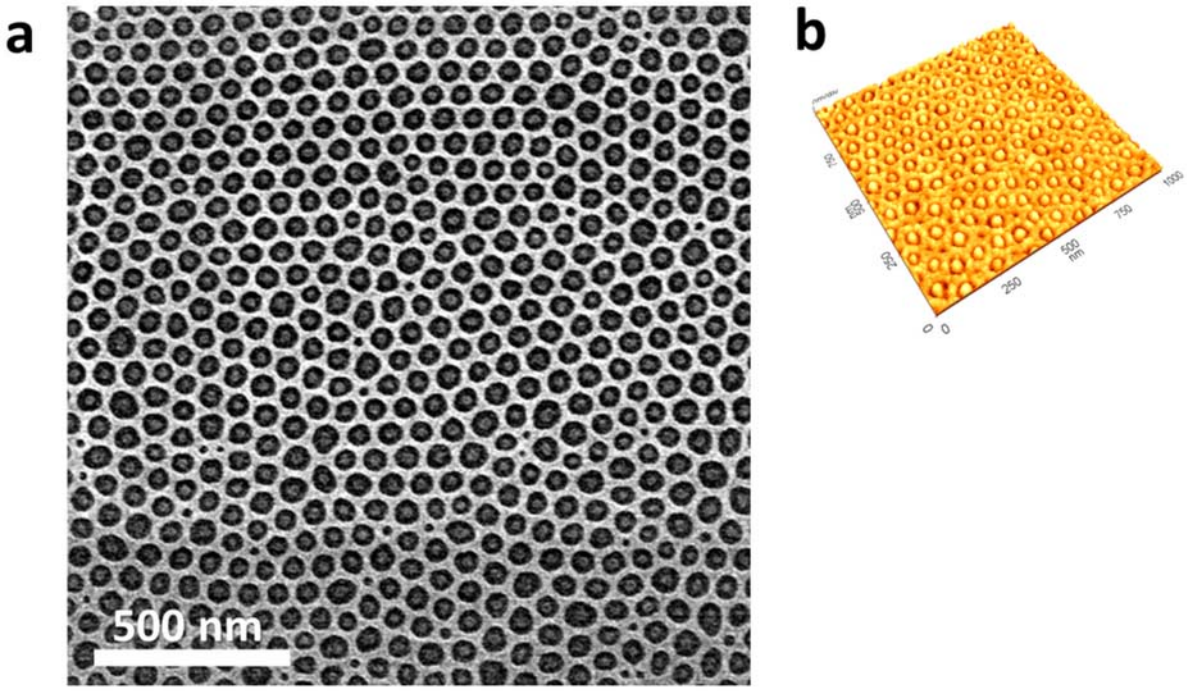


Figure 2.1-12 (a) A lower-magnification SEM image of the optimized hierarchical morphology. (b) AFM image (Park et al., 2013)

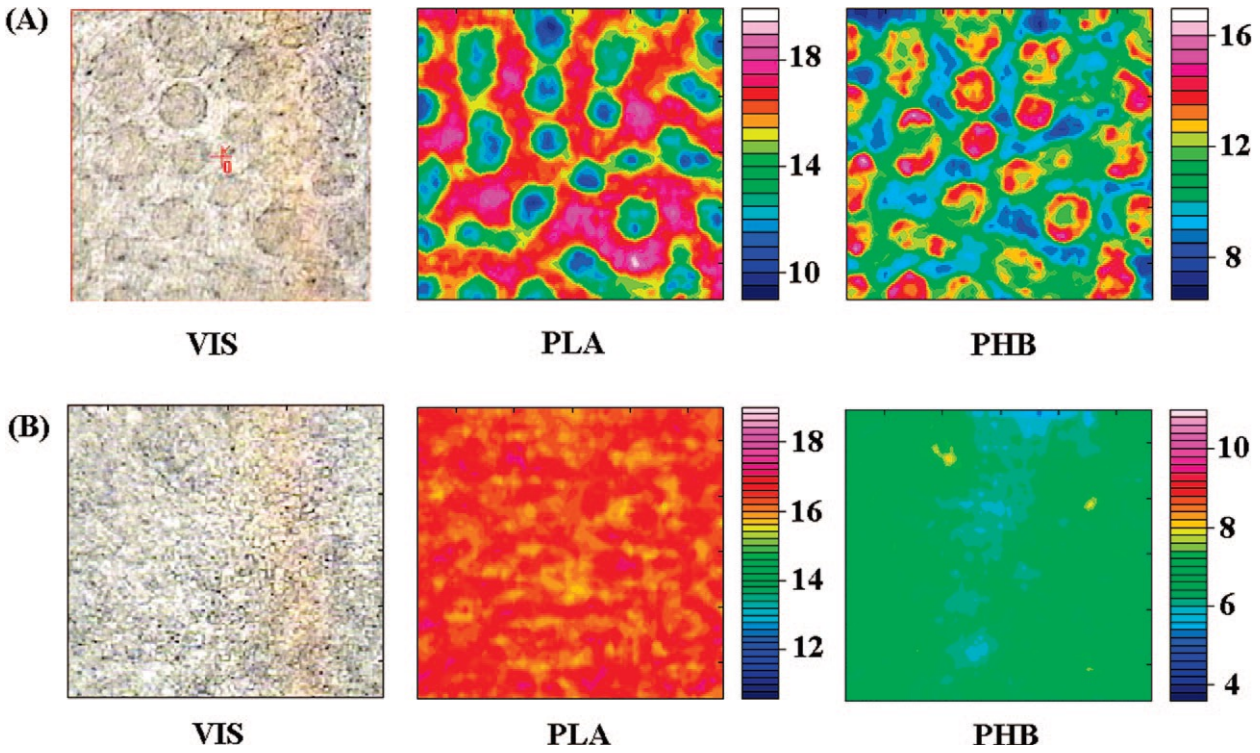


Figure 2.1-13 Visual image (left), PLA-specific FT-IR image (center), and PHB-specific FT-IR image (right) of a PHB/PLA (50:50% (w/w)) blend. (B) Visual image (left), PLA-specific FT-IR image (center), and PHB-specific FT-IR image (right) of a PHB/PLA (30:70% (w/w)) blend.(Vogel et al., 2008a)

ATR-FTIR technique has been also used by some researchers to investigate the phase separation of blends by detection of absorption band of different chemical groups in each phase. (Vogel et al., 2008a) Vogel et al. have shown that the absorption of C=O bond in the structure of polyester has detectable absorption band for the ATR-FTIR analyzer, which can be used to detect the phase separated structure in their blends. The peak of absorption for this blends will change gradually as a function of concentration. This is discussed in more details in section 2.2-5.

d Self-adhesion of polymeric films and their blends (Heat sealing, Hot-tack)

Heat Sealing is a thermal process of joining two polymeric surfaces, in intimate contact, at a practical combination of temperature, pressure and time, called seal temperature (T_s), seal pressure (P_s) and Dwell time respectively. (Theller, 1989) The source of heat makes practical difference in heat-sealing process. The choice of the heat source can have significant effect on the cost of process, although the material behavior is important during the sealing process, it is the

heating process that controls the production speed. (Najarzadeh & Ajji, 2014b) Heat can be supplied by electrical impulse and use of resistance wires. When a polar sealant is chosen, the heat can be provided by alternating electrical field. Other sources of heat may include laser radiation or friction caused by ultrasound vibration. Finally, in some special cases were the material is soft enough at room temperature, the seal can be achieved by exerting a high pressure on contact surfaces. (Hernandez et al., 2000)

The most common technique is the use of conductive sealers or heated sealing bars, as shown in Figure 2.1-14, which utilizes metallic bars using heating elements with adjustable temperature. These heated bars (jaws) are usually coated with non-stick materials. The two film surfaces will be pressured by these jaws and sealed.

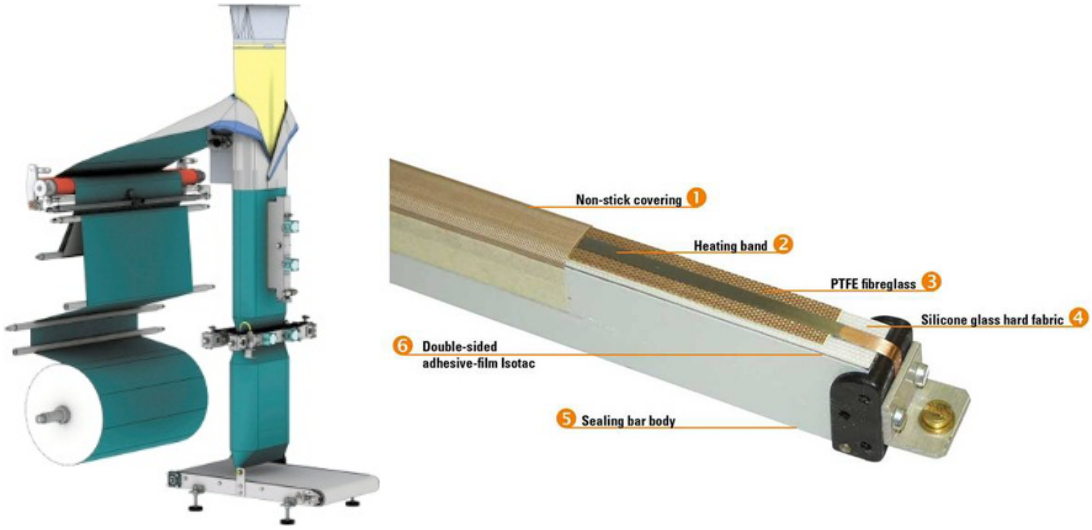


Figure 2.1-14 Left: Vertical Form-Fill-Seal Bagging Machine With heat seal Jaws (http://www.pkgsys.com/products/packaging-and-bagging/vertical-form-fill-seal-bagging-machine-mk); Right: Sealing bar (http://www.joke-fs.de/This-is-how-it-works.727.0.html?&L=3)

This type of heat sealing with heated bars for biodegradable resins is the one of interest in this study. Jaws design for this type of heat sealing machines can affect the strength of the sealed area. (Hernandez et al., 2000; Theller, 1989) For the sake of simplicity, flat bars were used in this study.

Suggested molecular mechanism for heat sealing by Meka and Stehling (Meka & Stehling, 1994; Stehling & Meka, 1994) is still forming the main basis of knowledge of the heat sealing process of single layer films of semicrystalline polymers. For a semicrystalline polymer, as illustrated in Figure 2.1-15, both films are kept in intimate contact by means of heated bars.

Melting of the crystals while the pressure is applied on the seal area will help increase the molecular contact and, if the process is long enough, molecular diffusion through surfaces create new interfacial entanglements. These molecular bridges between the two surfaces will give strength to the seal. For semicrystalline polymers, achievement of maximum seal strength is reliant on the complete melting of the crystalline structure. In other words, the maximum seal strength is normally achieved for temperatures higher than the melting point of the used resins. Finally, if the films are let to be cooled down before testing of the seal strength, the crystals will form and the seal will strengthen to the maximum strength and can be indiscernible from the bulk of polymeric material.

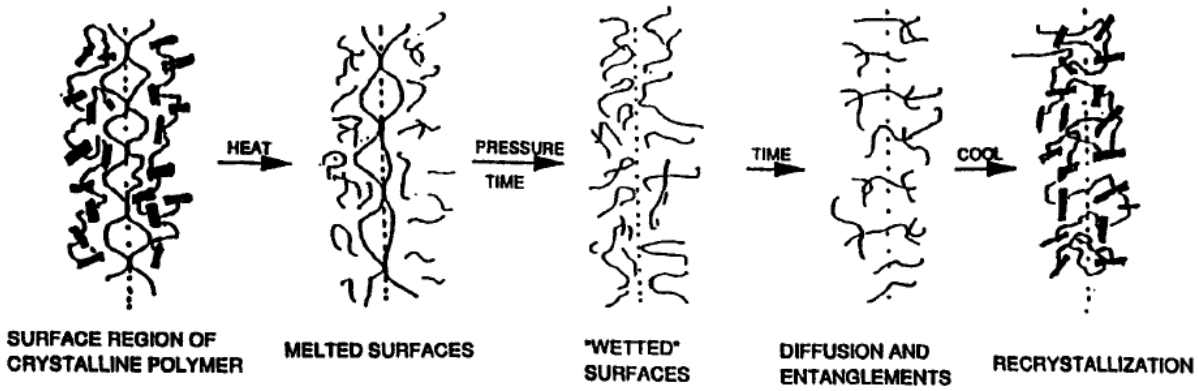


Figure 2.1-15 Postulated molecular process involved in heat sealing of semicrystalline polymer films(Stehling & Meka, 1994)

I Evaluation of a seal performance

Based on ASTM standards and published research works, evaluation of seal performance is endowed with the measurement of certain properties described henceforth. The strength of a seal is determined by the debonding force of two joined surfaces. Based on developed standards, this measurement can either be done after a negligible rest time when the polymer is still at the temperature of sealing process, called "hot-tack", or at practically larger rest time when the polymer has reached the ambient temperature and crystals have been formed, called "seal strength". (ASTM F88 / F88M-09 ,2009; ASTM F1921 / F1921M-12e1 2012)

- ***Seal strength measurement***

The force required to detach two sealed surfaces is measured as the strength of the seal. Where the measurement of seal strength is carried out for the adhered thin films, use of T-peel test is more customary. Two ends of the sealed area called "leg" are pulled in normal direction to

the plane of seal. The curve of (Force of adhesion/width) vs. (Length of separation) is illustrated in Figure 2.1-16 showing how force changes as the peeling of two surfaces continues.

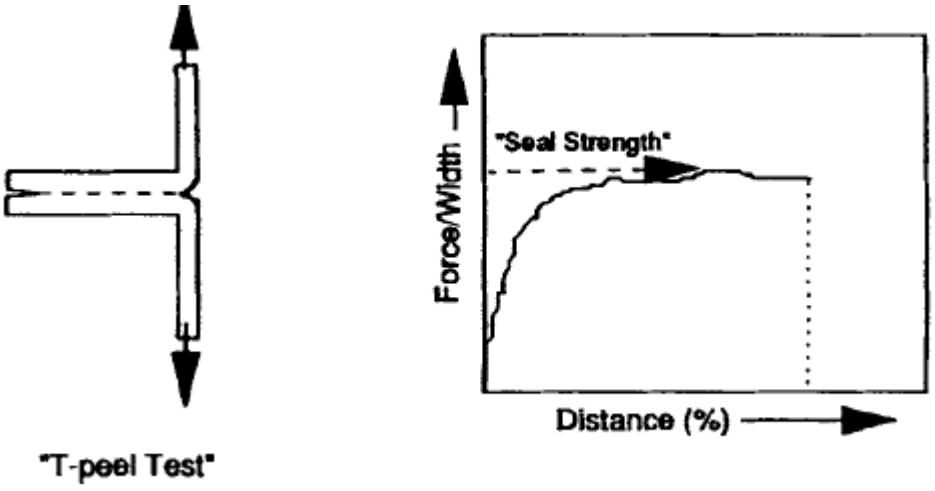


Figure 2.1-16 Schematic of T-peel test and obtained force-displacement curve(Meka & Stehling, 1994)

Depending on how resilient the seal is and the amount of interfacial entanglement and bridging, the mode of seal failure will be different. These failures will be discussed later. The more elongation the seal tolerates before complete failure and the stronger the seal is, the energy needed to break and separate the seal will be higher. This energy can be calculated from the area under the seal curve of tested films. (Meka & Stehling, 1994)

- ***Hot-tack measurement***

As explained earlier, the force measurement done right after seal formation indicates the adhesion properties at high temperature. This ability of seal to carry load at high temperature, hot-tack, provides opportunity for the design of many packaging processes. Measured hot-tack strength is normally lower than seal for a certain resin, although it can change significantly even between different grades of the same polymer. (Mueller et al., 1998; Najarzadeh & Ajji, 2014b; Qureshi et al., 2001) In seal measurement, solidification of the material results in stronger adhesion and higher seal strength.

Packaging processes in which the product is fed vertically into the package, hot-tack strength plays an important role. A schematic of a vertical form fill seal (VFFS) is given in Figure 2.1-14. The product weight exert a force on the bottom of the package while it is at temperatures close to the seal temperature and yet not solidified.

The response of seal to this immediate force, exerted right after sealing is the determining factor for the speed of the production line. Materials with low hot-tack strength will deform and fail as illustrated in Figure 2.1-17.

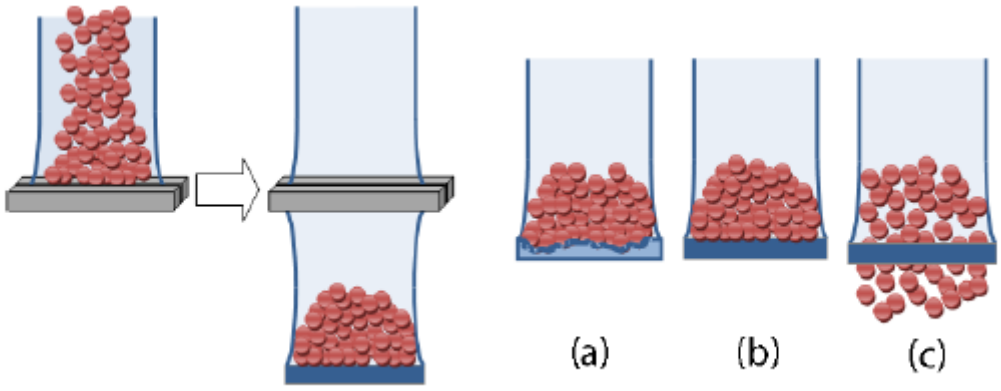


Figure 2.1-17 The schematic of weight bearing of seal in a VFFS process while it is still molten and hot (a) a deformed seal (b) a good seal (c) a weak seal with poor hot-tack (Najarzadeh & Ajji, 2014a)

When the product is fed horizontally, the package is usually carried on a conveyor belts that will support the weight of material. In these systems, which are called horizontal form fill seal (HFFS) and illustrated in Figure 2.1-18, hot-tack is still important. Coles et al. suggested in some cases that a minimum amount of hot-tack is needed to resist against the 'spring-back' forces in areas of package where the film is folded. (Coles et al., 2003)

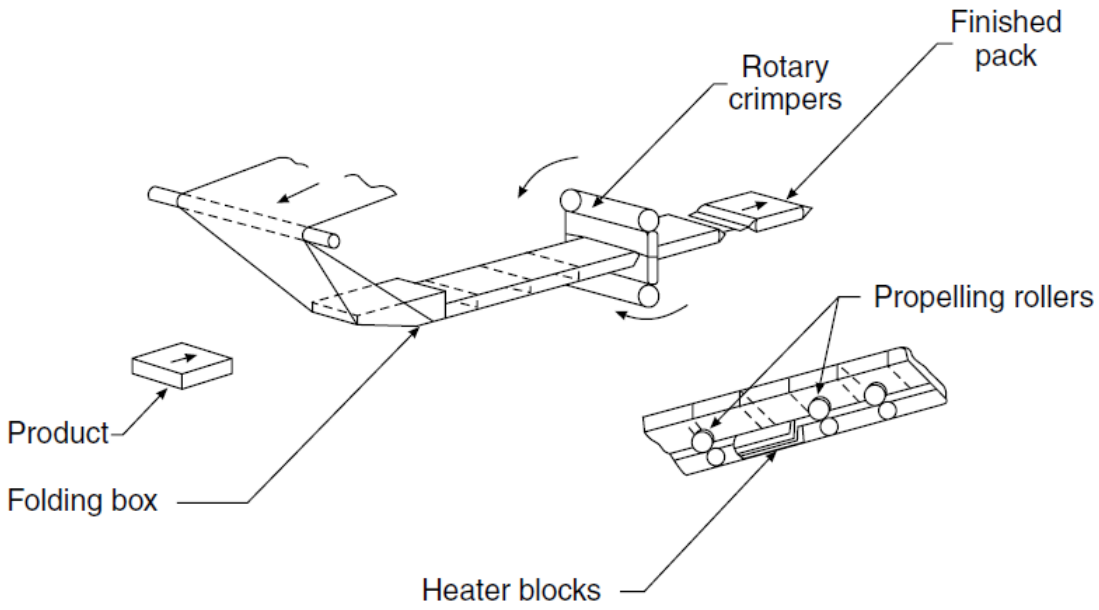


Figure 2.1-18 Horizontal form fill seal machine (HFFS)(Coles et al., 2003)

II Modes of failure in seal and hot-tack

Hermetic seals are important in order to secure the integrity of the whole package. Any type of failure in the seal can result in low performance and consequently the potential loss of the packaged product. As seal layers are normally part of a multilayer structure, these failures may not happen often in the seal area itself. Hence, any thermo-mechanical factor that could result in the failure of the seal will make the whole package weak and practically unusable.

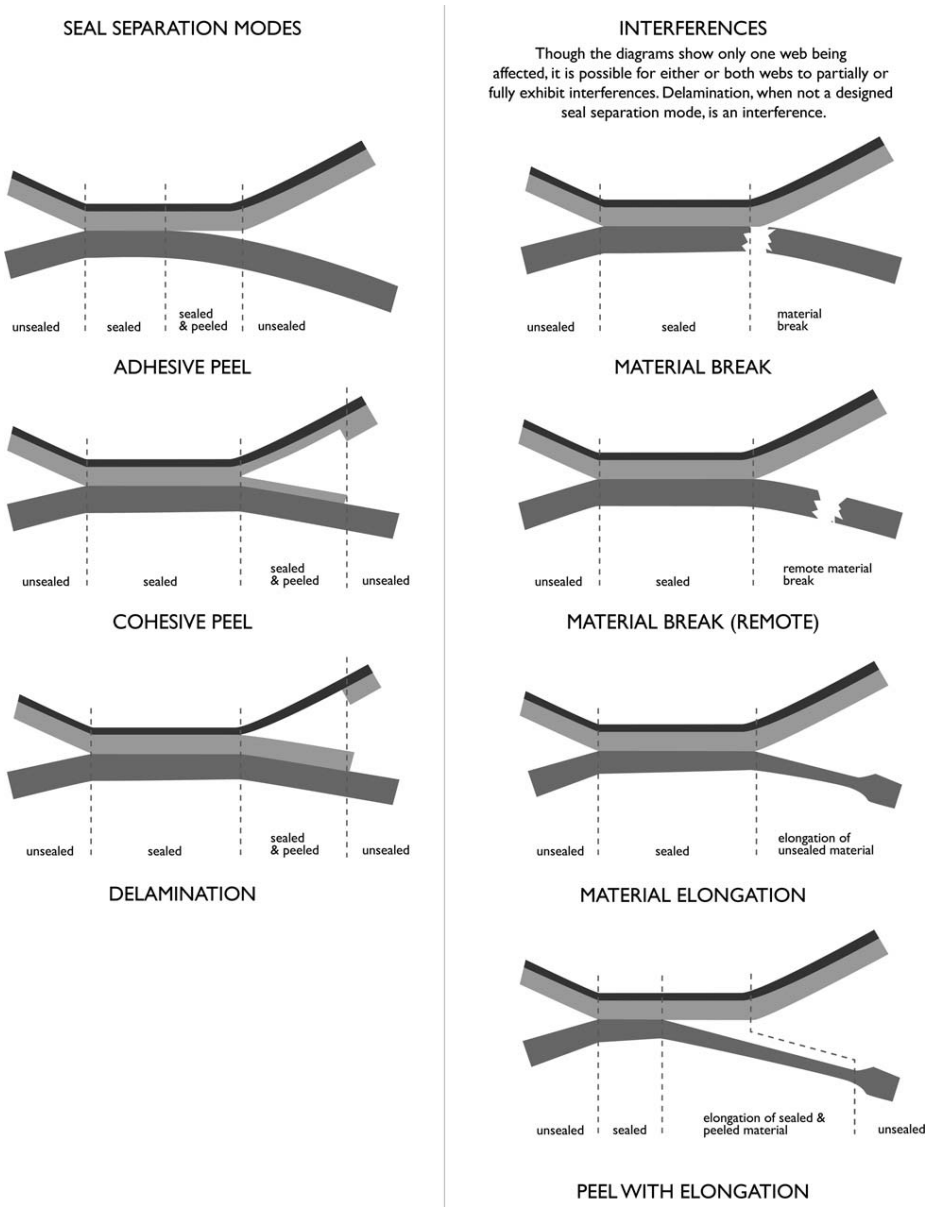


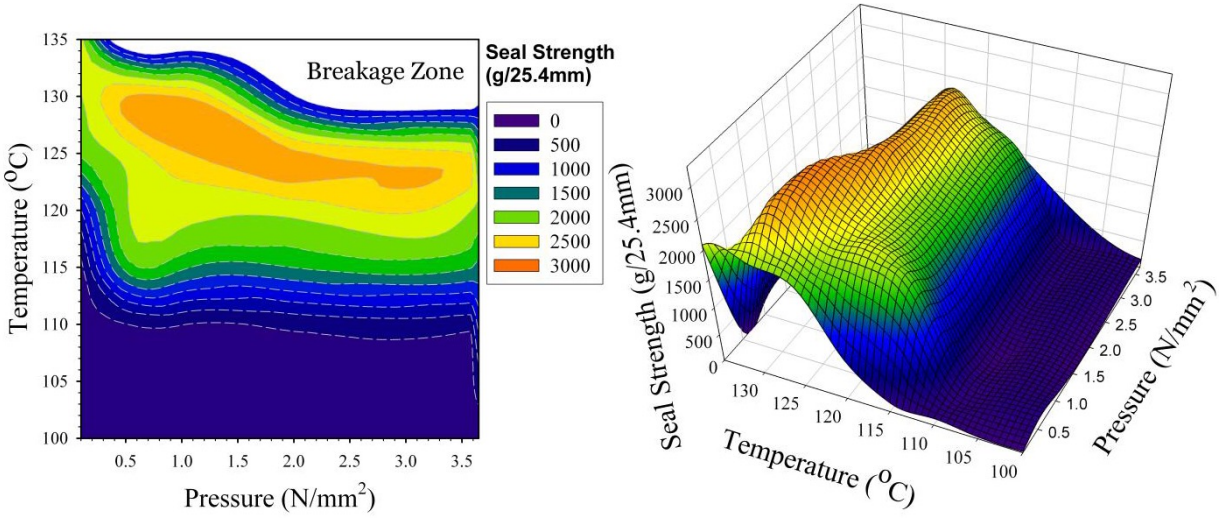
Figure 2.1-19 Schematic of the modes of failure of seal presented in ASTM test method (ASTM F1921 / F1921M-12e1 2012)

Peeling or adhesive failure mode usually happens right at the interfaces of seal layers when chains ends disentangle and surfaces part from the opposite surface; low temperature or short dwell time can cause this type of failure. Cohesive failure mode, occurs at high temperature and long dwell time which let inter-diffusion make strong enough seal to transfer the stress through the bulk of the seal layer. Delaminating failure mode is usually a failure caused by weak bonding in tie layer, which results in the separation of seal from the support layer. Breakage failure mode is happening at the seal edge where the seal becomes weak and the edges become

prone to tear. Break or tear in film's specimen might happen due to weak points on film or its support, distant from the seal area. The Elongation of the seal is usually related to hot-tack only as the material under the tension is still hot. Lower tensile strength results is elongated seal areas as are shown in Figure 2.1-19. (Najarzadeh & Ajji, 2014a)

III Effect of heat seal process conditions on seal characteristics

The conditions in which a heat seal is performed is a set of parameter such as temperature, dwell time and pressure as well as the type of heating sources and texture of the jaws. From these parameters, the heating source was fixed as mentioned before as the flat surface heating bars. The analysis of the effects of temperature and other parameters was discussed and evaluated for polyethylenes in previous research done in our group and a brief summary of the results is presented here. The interfering effect of time, temperature and pressure have been analyzed by Najarzadeh et al. and they have developed a guide map for sealing polyethylene based resins. The set parameters have been chosen based on this map. For simplicity of analyzing blends we used the range of parameters from guide map and combined them with some preliminary temperature window evaluation tests which will be discussed later. (Najarzadeh & Ajji, 2014b) Their study shows the significance of temperature and dwell time over the pressure of jaws, although a minimum pressure of 0.5N/m^2 is needed to ensure the quality of the seal.



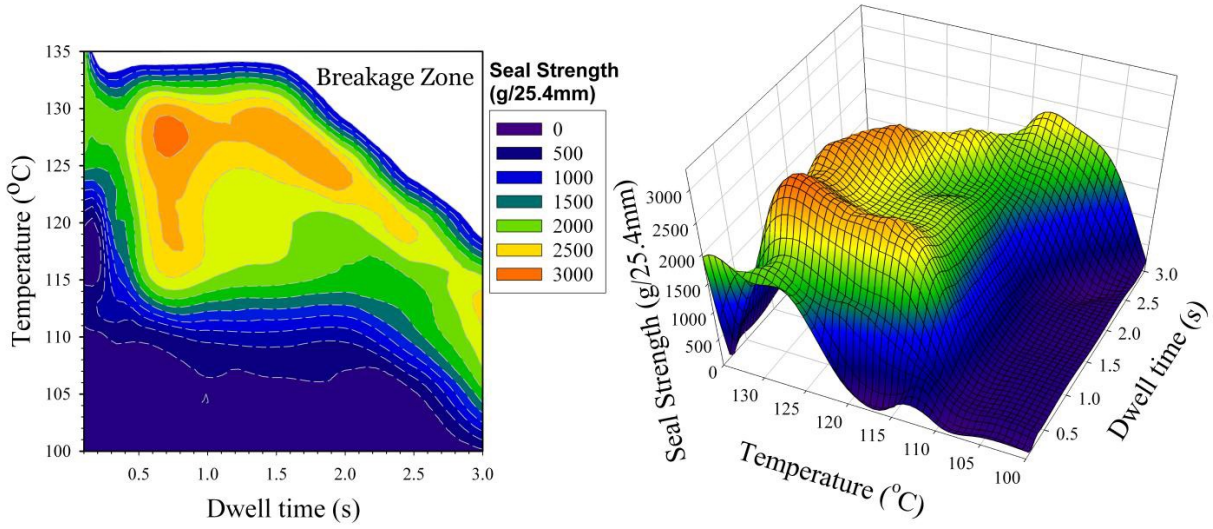


Figure 2.1-20 Top: Pressure-temperature dependence of seal strength in 3D and contour plots; Below: Dwell time-temperature dependence of seal strength in 3D and contour plots(Najarzadeh & Ajji, 2014b)

The conclusions of this study stressed that the time and temperature dependence of seal strength is a consequence of the amount of heat available in the interface of films, hence the choice of thinner layer with higher seal strength can provide with faster sealing and also higher rate of production as shown in Figure 2.1-20. (Najarzadeh & Ajji, 2014b)

The knowledge of the details of chemical structure (Mw, MWD, co-monomers, …) and chain branching have provided a wide choice of polyolefin resins (to be discussed later). The linearity of chains provided a higher diffusivity and stronger seals at lower temperatures, although branching can help provide wider operational window as illustrated in Figure 2.1-21. (Najarzadeh & Ajji, 2014a)

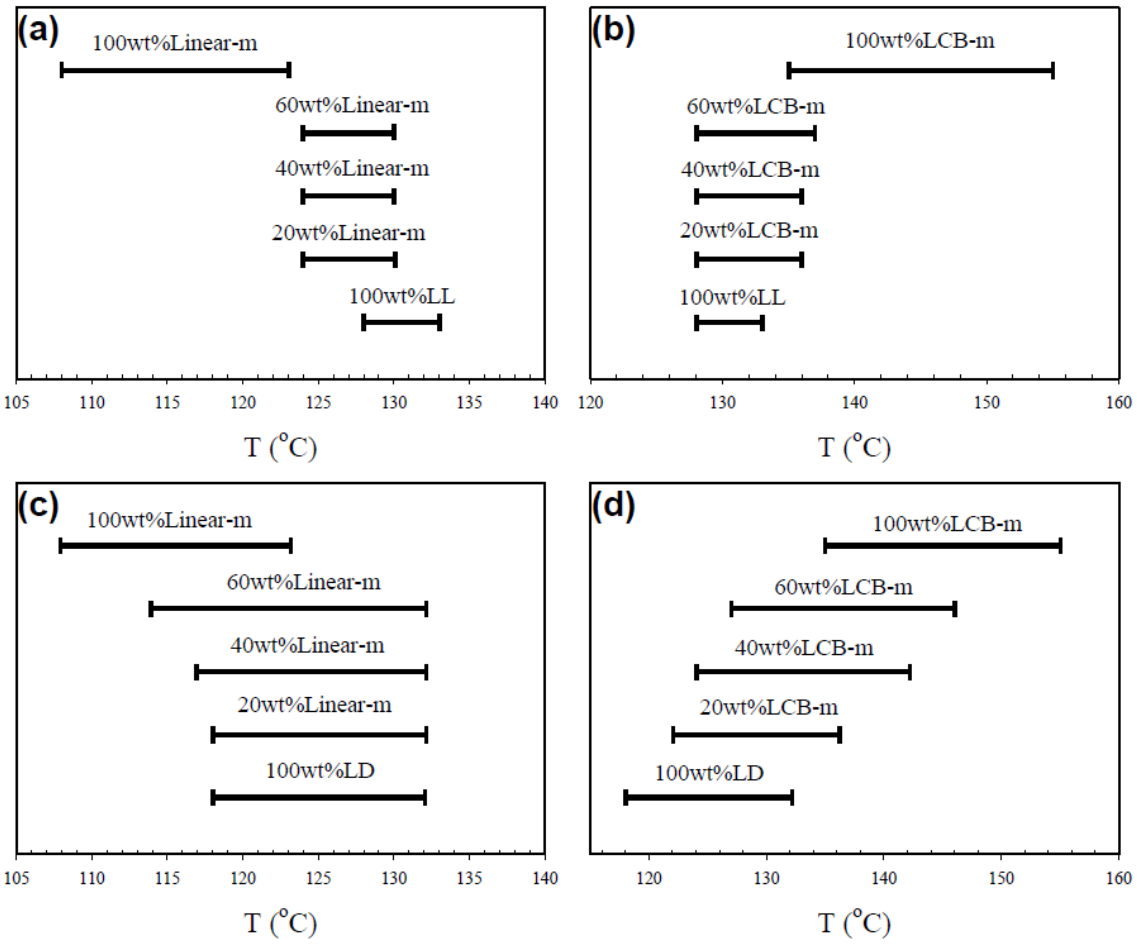


Figure 2.1-21 Adhesion strength plateau broadness for (a) LL/Linear-m blends, (b) LL/LCB-m blends, (c) LD/Linear-m blends, (d) LD/LCB-m blends (Najarzadeh & Ajji, 2014a)

e Seal layer material

Polyolefins have been the subject of attention of most researchers interested in seal and packaging processes. Although theoretically all type of thermoplastic materials, can be adapted for use in some seal and welding applications; flexibility, low T_g, acceptable mechanical and chemical properties as well as non-toxicity favor use of polyolefins for these applications. (Wagner, 2009) Biodegradable resins such as PLA, PCL and PBAT and some proteins have been used in retails applications and few research works tried to address their seal behavior (Auras et al., 2004; Gruber & O'Brien, 2002; Kim & Ustunol, 2001; Najarzadeh et al., 2014; Wagner, 2009) Although some works explained basic seal properties of pure and blended biodegradable

resins, no commercial seal grade of these resins, comparable to polyolefin based ones, have been yet developed.

Beside the works on polyolefins, some other studies on the improvement of seal behavior of resins with higher melting points were carried out by Boiko et al. (Boiko et al., 2001; Boiko & Prud'homme, 1999; Boiko & Prud'homme, 1998). They were able to shift the seal initiation temperature of PET by up to 17°C lower than its T_g.

Study of self-adhesion of PET by Boiko et al. was done using both semicrystalline and amorphous resins. Molten PET films were produced and annealed at 180°C and then used as is for the investigation on semicrystalline resin behavior. Quenched films in liquid nitrogen showed very low crystal content and were used as amorphous grade films. The samples were bonded in a lap-shear joint geometry at temperatures varying from 64°C (T_g-17°C) to 108°C (T_g+17°C) for contact times from 5 minutes to 15 hours, cooled to room temperature, and submitted to a tensile loading. (Boiko et al., 2001) Shear strength was calculated as the measured force at break divided by the contact area. Amorphous PET in the vicinity of its T_g showed a seal strength of one order of magnitude higher than that for semi-crystalline PET as indicated in Figure 2.1-22.

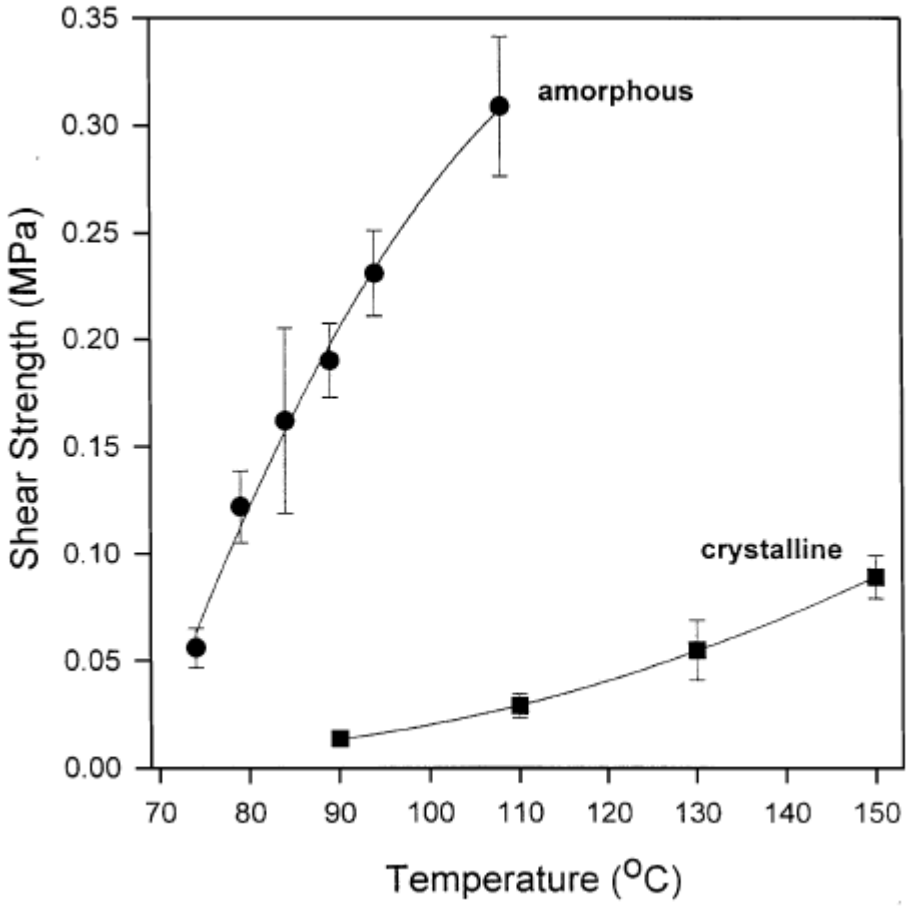


Figure 2.1-22 Shear strength as a function of healing temperature at amorphous/ amorphous and crystalline/crystalline PET (M=15000) interfaces. Healing time is 30 min (Boiko et al., 2001)

The fundamental findings on the effect of structure of the chain backbone and crystallinity on seal and hot-tack behavior of polyolefins mentioned above can be extended to other materials than polyethylene (PE) and polypropylene (PP) based resins. The comparable resins, based on the linearity of molecular chain, to linear metallocene PE can be PCL with its totally linear structure and for short branched PEs, PLA or PHB can be proper selections. A comparison of the effect of crystallinity and chain mobility can be done by replacing PCL with PBAT in the blends and using quenching technique, which will be discussed in detail thereafter. For the purpose of this study, a number of biodegradable polyesters and aromatic co-polyesters were selected and analyzed, which are presented in following chapters.

2.2 Biodegradation of plastics

The objectives of this study are not only the improvement of the properties of these resins, through deep understanding of their chemical and physical characteristics and their combination with processing technique, but it is also important that the final compostability and rate of biodegradation of these biodegradable plastics be studied and improved. Biodegradation rate may vary depending on many factors such as chemical structure, blending, microbial activity of compost, the choice of degradation process (either aerobic or anaerobic) and the degradation condition such as temperature, humidity and depth of burial. (Ahn et al., 2011; Ganjyal et al., 2007; Ghorpade et al., 2001; Hakkarainen et al., 2000; Kale et al., 2007; Madhavan Nampoothiri et al., 2010; Mulbry et al., 2012; Nampoothiri et al., 2010; Ochi, 2008; Pradhan et al., 2010; Pushpadass et al., 2010; Sarasa et al., 2009; Tosin et al., 1996)

Based on the ASTM standard (ASTM D6400 2012), for a bioplastic to be compostable, it needs to degrade in the composting setup and lose 90% of organic material in its structure within 180 days. House yard composting systems usually have slower rate of degradation than controlled industrial systems. Besides, for some synthetic and natural polymers such as polyethylene, polypropylene and natural rubbers an oxidative disintegration step is required before the polymer becomes readily biodegradable. This separate disintegration step will account for a prolonged conversion of material to CO_2, water and biomass, which will exceed the time limit required by compostable polymers' standards. (Arvanitoyannis, 1999)

2.2.1 Standards and norms in analysis of compostable plastics

There are several reviews on biodegradability of polymers and mechanisms involved in their biodegradation and composting. (Avérous, 2004; Briassoulis et al., 2010; Gallardo-Lara & Nogales, 1987; Garlotta, 2001; Grima et al., 2000; Hasunuma et al., 2013; Lucas et al., 2008; Shah et al., 2008) An extensive review of standards, designed to evaluate and perform biodegradation and composting of polymers, was performed by Briassoulis et al. Both aerobic and anaerobic degradation standards have been investigated in their works. (Briassoulis & Dejean, 2010; Briassoulis et al., 2010)

For the purpose of this study, two standards to analyze the composting behavior of plastics were considered: "Specification for Labeling of Plastics Designed to be Aerobically

Composted in Municipal or Industrial Facilities" (ASTM D6400 2012) and "Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, Incorporating Thermophilic Temperatures". (ASTM D5338 2011) ASTM D6400 is mainly a guideline to which standards and procedures are to be followed and the main methodology is given in ASTM D5338-11. The composting process is a microbial active degradation which is accelerated by controlling the humidity, temperature and the inlet of oxygen in the system. As compost is obtained in batch, the quality of compost is to be determined periodically to make sure that its properties have not changed through the testing period.

2.2.2 Compost quality

"Compost is an organic soil conditioner obtained by biodegradation of a mixture principally made up of various vegetable residues, occasionally with other sub- organic material, and having a limited mineral content." (Grima et al., 2000) The compost composition and its ratio of minerals can affect the composting time of biodegradable plastics. (Briassoulis et al., 2010; Gallardo-Lara & Nogales, 1987; Kale et al., 2007; Pushpadass et al., 2010; Tosin et al., 1996) More specifically, the ratio of N/C has been mentioned by some researchers, to have the most important effect. Tosin et al. hypothesized that Nitrogen plays a determining role from the analysis of the local shortage of nitrogen in the solid substrate due to its consumption and low diffusion from neighboring compost, which account for slower degradation of Starch based biomaterials. (Tosin et al., 1996) Nitrogen ratio in the compost can be adjusted by addition of ammonia. (Briassoulis et al., 2010; Kale et al., 2007)

For composting of plastics, there are some recommendations about the properties of compost. (Briassoulis et al., 2010; Pradhan et al., 2010; Tosin et al., 1996) Due to the regulations imposed by "*Soil Protection and Contaminated Sites Rehabilitation Policy: APPENDIX 2 / Generic criteria for soils and groundwater*" of Quebec, compost should not contain metals and metalloids of certain type and concentration, as give in Table 2-6. "The A criteria presented in the 1988 policy grid for metals and metalloids were compared to the distributions of background levels calculated by the ministère des Ressources naturelles (MRN). The values allotted to the criteria are generally of the order of the 90th percentile of the distributions". (Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques 2005)

Table 2-6 Background levels (A criteria) for metals and metalloids B: St. Lawrence Lowlands Sector A: Appalachians Sector G: Grenville Sector S: Superior and Rae Sector F: Labrador Trough Sector

Metals and Metalloids	Background Levels (A criteria) mg/kg (ppm)
Silver (Ag)	B: 2 A: 0.8 G: 2 S: 0.5 F: 0.8
Arsenic (As)	B: 6 A: 15 G: 10 S: 5 F: 10
Barium (Ba)	B: 200 A: 265 G: 200 S: 200 F: 245
Cadmium (Cd)	B: 1.5 A: 1.3 G: 0.9 S: 0.9 F: 1.5
Cobalt (Co)	B: 15 A: 20 G: 15 S: 20 F: 25
Total chromium (Cr)	B: 85 A: 75 G: 45 S: 85 F: 80
Copper (Cu)	B: 40 A: 50 G: 50 S: 50 F: 100
Tin (Sn)	B: 5 A: 5 G: 5 S: 5 F: 5
Manganese (Mn)	B: 770 A: 1000 G: 1000 S: 1000

	F: 1000
Molybdenum (Mo)	B: 2 A: 2 G: 6 S: 6 F: 6
Nickel (Ni)	B: 50 A: 55 G: 30 S: 50 F: 100
Lead (Pb)	B: 50 A: 40 G: 50 S: 40 F: 30
Selenium (Se)	B: 1 A: 3 G: 3 S: 3 F: 1
Zinc (Zn)	B: 110 A: 130 G: 100 S: 120 F: 230

The pH of the compost is to be adjusted in the range of 6-8 to maintain the optimum microbial activity and the humidity must be set to 60% of water retention capacity of compost.(Briassoulis et al., 2010; Kale et al., 2007; Pushpadass et al., 2010; Tosin et al., 1996) Water retention capacity is the maximum absorbable water by compost normalized to the total mass of dry compost. Water retention capacity can be determined by soaking the compost in excess amount of water and subsequent filtration. Measurement of mass of filtrate before and after drying gives the water retention capacity of the compost. To adjust the water content of compost consideration of water content of compost as received, is necessary.

2.2.3 Composting setup

A laboratory scale composting setup is shown in Figure 2.2-1. The operational parameters involved are temperature (55-65 ºC) and ratio of compost to biodegradable plastic (≈6). Evolved CO_2 can be collected and measured using different techniques, such as gas chromatography and titration. Based on ASTM standard, the titration can be done in saturated solution of $M(OH)_2$, where M is of the metals of second groups. Sample calculation of evolved CO_2 gas using a

solution of $Ba(OH)_2$ is determined as follows. (ASTM D5338 2011) (Following calculation is given by ASTM test method)

Form the carbon content of the material used, the amount of theoretical CO_2 will be determined.

If a material has *w*% carbon then,

$$\frac{w}{100} * g\ of\ material\ charged = Y\ g\ carbon\ charged\ to\ compost\ vessel = C_i \quad eq\ 2.2-1$$

$$C + O_2 \longrightarrow CO_2 \quad eq\ 2.2-2$$

$$12g\ C\ yeilds\ 44g\ CO_2 \checkmark \quad \text{eq } 2.2-3$$

Then the reaction with the base solution and titration with acid will be:

$$Ba(OH)2\ +\ CO2 \square BaCO3\ +\ H2O \quad eq\ 2.2\text{-}4$$

$$Ba(OH)2\ +\ 2HCl \square BaCl2\ +\ 2H2O \quad eq\ 2.2-5$$

Number of moles of CO_2 produced:

$$moles\ of\ CO2\ =\ moles\ of\ Ba(OH)2\ at\ start - \frac{moles\ HCL}{2} \quad eq\ 2.2-6$$

$$\%\ biodegradation\ =\ \frac{(mean\ Cg\ (test) - mean\ Cg\ (blank) \square 100)}{(\ C_i * \frac{44}{12})} \checkmark \quad eq\ 2.2-7$$

Where:

C_g = amount of gaseous-carbon produced, g, and

C_i = amount of carbon in test compound added, g.

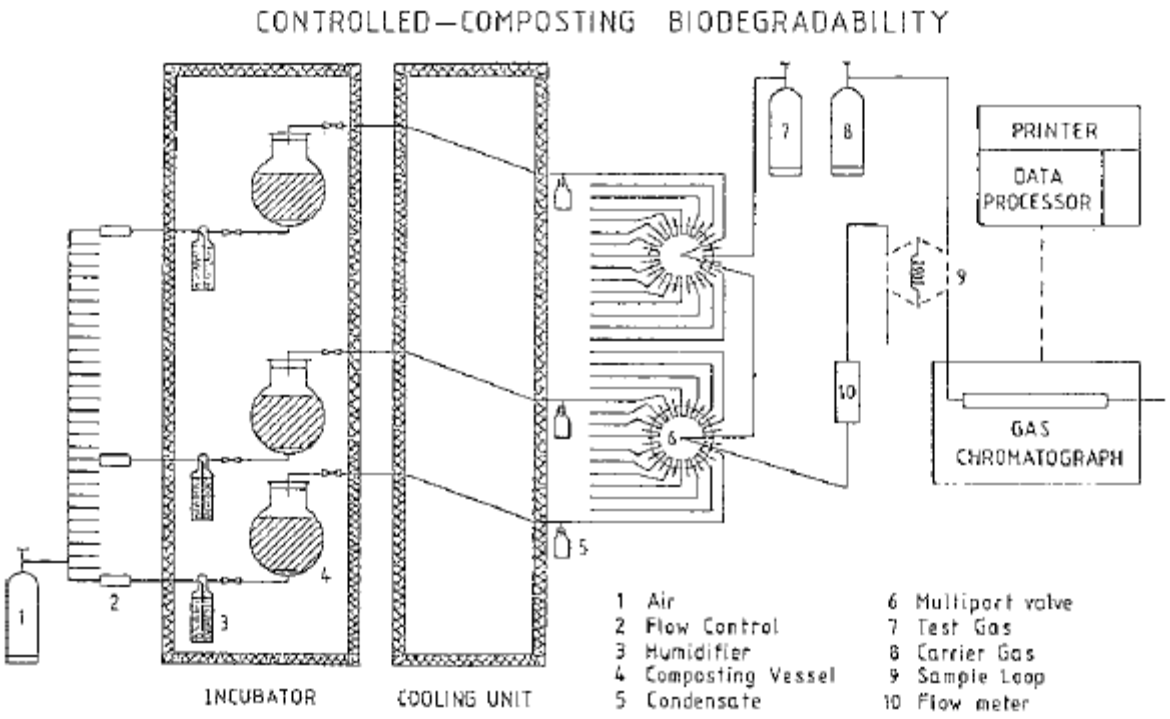


Figure 2.2-1 Optional composting setup using gas chromatography (ASTM D5338 2011)

2.2.4 Disintegration of biodegradable plastics

Beside mineralization degree, which is conversion of content of carbon in organic material to CO_2, the rate at which the polymeric article disintegrate is very important. (ASTM D6400 2012) For polymeric films, large surface area may be problematic in landfill and waste management systems. Illustration of disintegration of PLA bottles in composting condition is given in (Kale et al., 2007). They have shown the capability of composting to disintegrate PLA at a very convenient rate and studied the effect of composting parameter on the biodegradation of PLA bottle which will be discussed later.

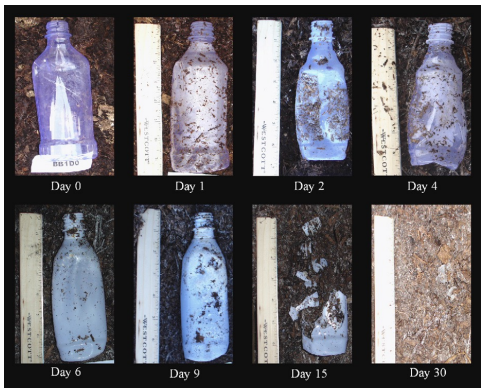


Figure 2.2-2 Biodegradation of PLA bottles in real composting conditions.

For polymeric blends, some published studies reported prolonged disintegration times but no detail of the involved mechanisms have been provided as shown in Figure 2.1-1. (Grima et al., 2000; Weng et al., 2013)

The understanding of the mechanism of change during the disintegration process of biodegradable blends require the development and use of instrumental and spectroscopic techniques that can follow the chemical changes of the material.

3.1.1 Detection techniques

Through degradation, the backbone of polymeric chain will break to lower molecular weight species either by hydrolytic degradation or enzymatic digestion. Aliphatic polyesters behave differently, based on the structure of their repeating groups. For PLA, hydrolysis has been suggested as the main degradation step. (Auras et al., 2004; Grizzi et al., 1995; Kale et al., 2007; Siparsky et al., 1998) PHAs are a group of aliphatic polyesters which are less prone to hydrolysis but, as these polymers are produced through microbial activities, many bacteria have developed enzymes to break and digest their molecular structure. For the rest of biodegradable polyesters, mixed mechanisms of hydrolytic and microbial digestive degradation have been suggested. (Shah et al., 2008)

For pure materials, the change in molecular weight or development of their oligomeric and monomeric species were monitored by many researchers. Gel permeation chromatography (GPC) was used successfully to determine the change in molecular weight of pure samples through degradation.(Agarwal et al., 1998; Cossu et al., 2011; Grizzi et al., 1995) An illustration of the change in the molecular weight of PLA after several weeks of degradation is shown in Figure 2.2-3.

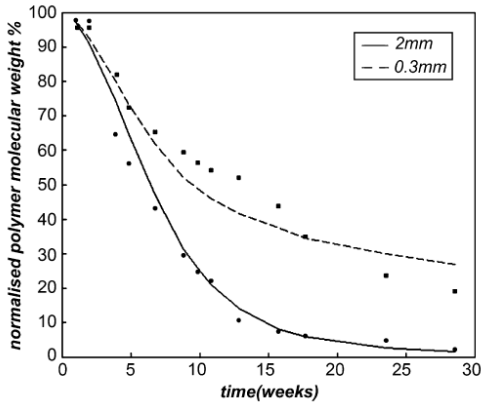


Figure 2.2-3 Comparison between the predicted (lines) and experimental (discrete symbols) ester bound concentration (averaged over the plate volume) as functions of time for two plates of different thickness. (Grizzi et al., 1995; Wang et al., 2008)

For polymers for which the measurement of this change is not possible, due to blending and insolubility problems, the use of a composting setup can give a cumulative rate of change in the weight of the material. (Grima et al., 2000; Lucas et al., 2008; Shah et al., 2008) Measurement of residual weight can also give the general insight into the how significant the rate of degradation of these resins is. To our knowledge, no detailed study of the change in concentration and structure of biodegradable blends have been published and there is a need for deeper understanding of the degradation mechanisms in biodegradable blends.

ATR-FTIR spectroscopy is a successful technique in the determination phase separation and composition of blends. This technique, together with the right choice of reference absorption bands can also be useful in following the change in the chemical structure of pure resins. FTIR technique have been also used to follow the change in the chemical structure of polymers after degradation. Few works address the successful use of FTIR in following degradation of pure biodegradable plastics after composting.(Agarwal et al., 1998; Cossu et al., 2011) As explained before, PLA degradation is a sequence of hydrolysis step followed by microbial biodegradation. Braun et al. suggested an improved methodology to analyze lactides residue in PLA for medical application. (Braun et al., 2006) In the case of PLA, the residual lactide has a characteristic absorption peak that is not found in PLA itself and is due to the COO breathing mode. Absorption of the carbonyl group in PLA also has a shift toward higher wavenumbers. The insertion of a monomer into PLA will give rise to a shoulder absorption peak which become stronger in proportion to the increase in lactide concentration.

The calculation of the concentration of monomer will be then possible by taking into account the area of absorption of each band related to the PLA and the lactide.

Here, Beer's law (eq 2.2-8) can be used as the basis of calculation and the equation can be expanded to be used for a mixture of PLA and lactides taking both absorption characteristic of PLA(λ_p) and absorption characteristic of monomer (λ_l) to obtain (eq 2.2-9) and calculate the ratio of absorptions, which gives concentration of each component.

$$A(\lambda) = \varepsilon(\lambda) l c \qquad eq\ 2.2-8$$

$$\frac{A(\lambda_l)}{A(\lambda_p)} = \frac{c_{l,\lambda_l} e(l,\lambda_l)}{c_{l,\lambda_p} e(l,\lambda_p) + c_{l,\lambda_p} e(l,\lambda_p)} \qquad eq\ 2.2-9$$

The gradual change in the absorption bands, as shown in Figure 2.2-4, can be fitted to obtain a calibration curve to analyze the ratio of absorption to real concentration of PLA and monomers.

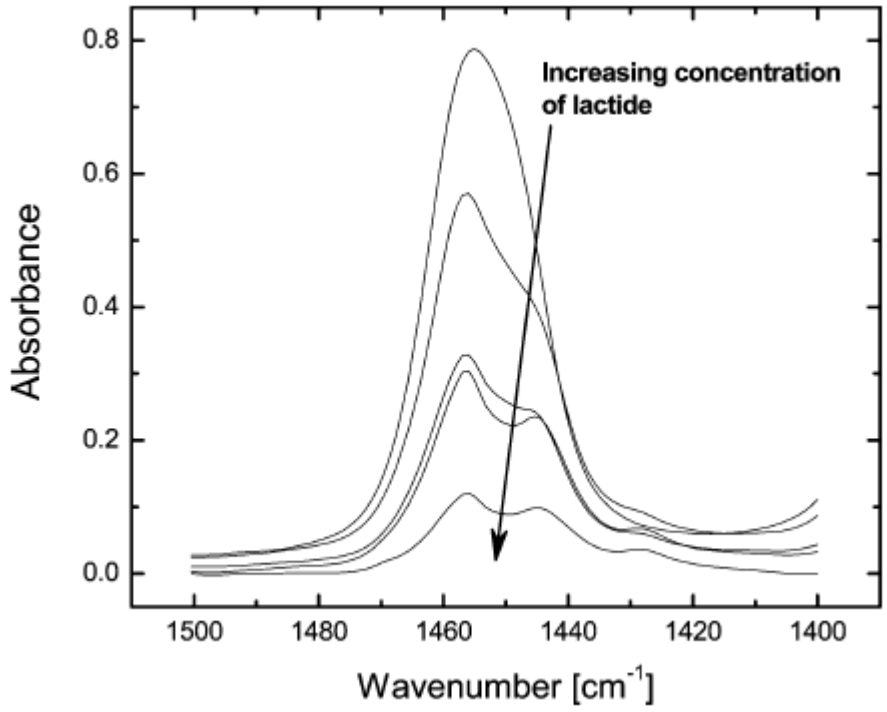


Figure 2.2-4 Spectral region between 1520 and 1400 cm^{-1} showing the formation of a double peak of medium intensity with increasing lactide concentration in a binary blend of lactide and PLA accompanied by a decrease in absorbance. Infrared spectra are shown for 100/0-P/L, 60/40-P/L, 40/60-P/L, 20/80-P/L, and 0/100-P/L.(Braun et al., 2006)

Considering the above mentioned applications and the fact that the C=O stretching bond for different polyesters are devisable in FTIR spectrum, the ATR-FTIR technique, this can be

used to follow the change in the concentration of blends of biodegradable polymers and specifically the hydrolysis step in PLA degradation and will be utilized in this study.

2.3 Originality of the work

Considering the above literature review, we have come to the conclusion that heat sealing of biodegradable resins has not been well studied and there is a lack of knowledge on the behavior of these resins in the seal process. Understanding of the behavior of the biodegradable resins is essential in the design of cost effective and processable seal layers for industrial applications.

Blending will affect the characteristics of a seal layer. Blends of biodegradable materials have been rarely studies for this application and the understanding of crystallinity and morphology of these blend is a requirement to enhance self-adhesion of films made from them. Crystallinity of these resins affect also significantly the seal process and a detailed study of the crystalline structure and content is very important as it will affect the design of a seal layer with improved seal behavior. Understanding of the importance of crystal content of films on their self-adhesion behavior and development of blends with different crystallinity will help in providing a wide temperature window and safe processing range.

Compostability of blends can be an issue as the hydrolysis rate and microbial action on the blends would differ from pure resins. Few works addressed the possibility of different hydrolysis mechanisms in blends of biodegradable plastics. Little knowledge of composting behavior of these blends have been developed and these works have not studied the behavior of each phase in binary of multiphase blends. Understanding of selectivity of degradation of separate phases and the rate of hydrolysis of each component will be a significant progress in the design of compostable packages form these blends.

2.4 Objectives of current Study

The main objective of this study is:

“Development of biodegradable seal layers from blends based on biodegradable plastics and understand their degradation for sustainable packaging applications”

To achieve this goal the specific objectives were designed:

- Production of processable biodegradable blends based on PLA, PHB, PCL and PBAT through melt compounding and development of sealable films by means of cast film techniques.
- Establishment of a correlation between the composition, morphology and crystallinity of blends with their self-adhesion properties.
- Assessment of a comparative study of the performance of these blends with conventional olefin based seal layers.
- Development of a composting setup and a reliable test protocol to analyze the degradation byproducts of films in simulated composting conditions. Analyze and evaluation of blend of PLA/PBAT and PHB/PBAT as test samples in terms of composting and degradation rate and selectivity of compost condition on biodegradation of phases of blends

CHAPTER 3 METHODOLOGY

The experiments that were carried out in this thesis have been performed in subsequent phases as follows:

Raw material selection and characterization of raw materials was an essential step, which included the use of Differential Scanning Colorimeter (DSC) instrument for thermal analysis and determination of melting point and glass transition temperature (T_g) of the resins. And also in this phase we carried out rheological measurements of the neat resins. Processing and comparison of single layer films was also part of the first phase of this thesis.

The first phase was followed by the blending of virgin resins and the analysis of mechanical, thermal and seal properties of blends and determination of effect of morphology of obtains samples on their said properties. These steps followed by the use of quenching technique and removal of crystalline phase of blends. The used of seal test machine helped facilitation the measurement of self-adhesion properties both in elevated and at ambient temperatures.

In the last phase a combination of FTIR spectroscopic analysis and composting setup were made use to follow the change in the structure and mechanical behavior of virgin samples and blends. Determination of the rate of biodegradation of the samples was made possible using a titration method to neutralize the evolved CO_2 from composting setup.

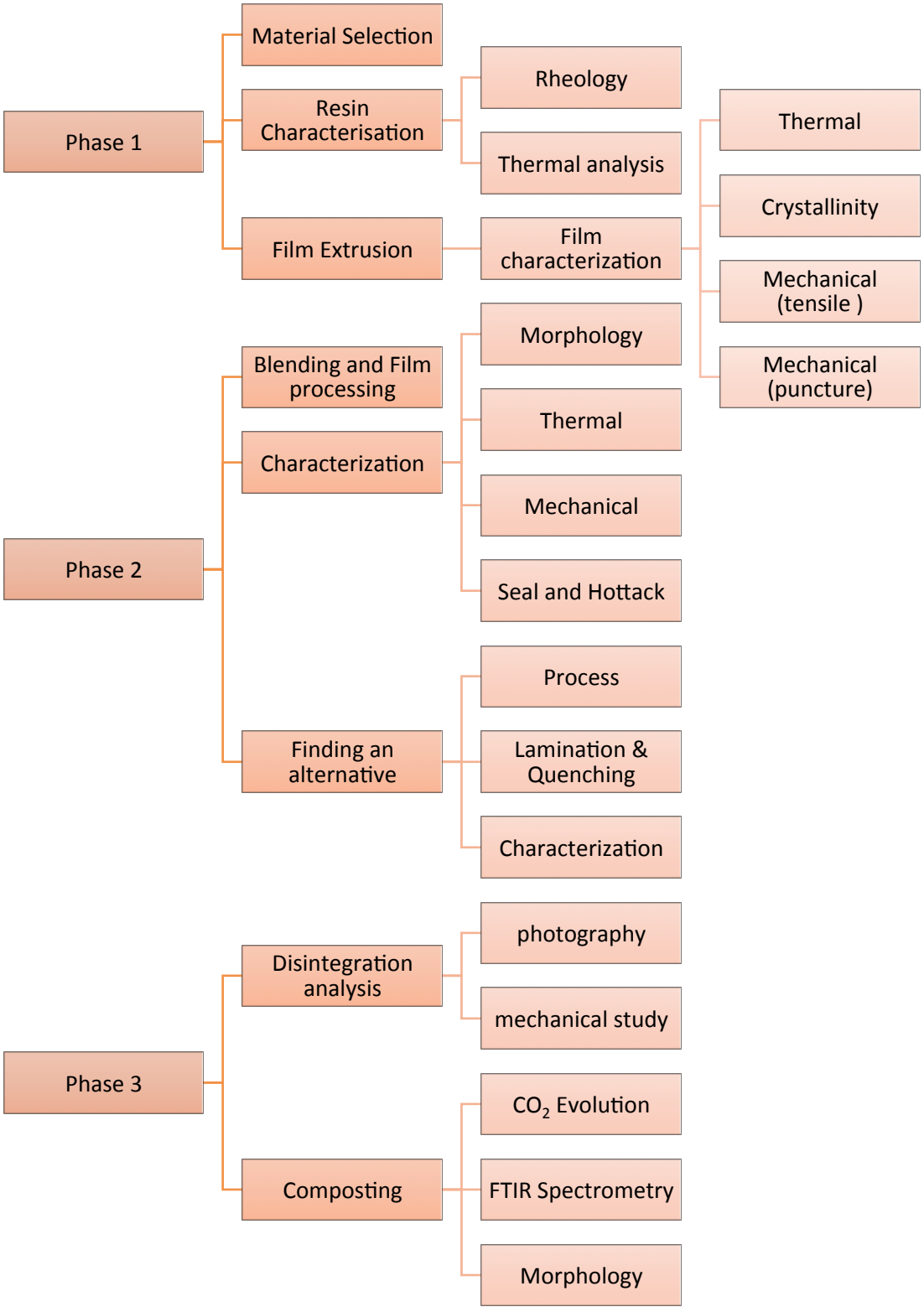


Figure 3-1 Experimental strategy

3.1 Materials

The seal grade Polylactide (PLA) 4060D obtained from Natureworks, Cargill DowLLC. USA, is a copolymer of D&L lactide with about 10 mole percent D-monomer content which is considered to be an amorphous grade. A film grade PLA resin 4032D, from Natureworks, has been used for lamination applications. The Poly-ε-caprolactone (PCL) CAPA grade was purchased from Solvay LLC USA. The Poly (butylene adipate-*co*-terephthalate) (PBAT) was provided as commercial grade Ecoflex FBlend C1200 by BASF, USA. The Polyhydroxybutyrate (PHB) commercial grade P209 was obtained from Biomer, Germany.

Some of the material's characteristics are listed in .

Table 3.1-Material's characteristics

	PLA 4060D	**PHB**	**PCL**	**PBAT**
Elongation at break, in %	4-10	6-10	>500	>500
Glass transition temperature	62	1	-61	-30
Opacity (Films)	0.99	7.64	8.68	6.23
Biodegradation* Mineral ization in %	100	100	100	100
Surface tension (g) in mN/m.	50	53	51	55
γ^d(Dispersiv component)	37	42	41	43
γ^p (Polar component)	13	11	10	12

Film sample of pure material as well as their blend in a wide range of concentrations have been made. These samples used to cover wide operation window in term of mechanical and seal

properties. All the samples have been processed in twin-screw extruder (Leistritz model ZSE 18 HP co-rotating) and were made into films using a cast film die. The film width is about 25cm. All the films have been drawn from the melt to a thickness of 30 μm for further analysis.

The temperature profile of the extruder and dies varies based on the pure resin for the comparison process we kept the extruder temperature profile at the temperature profile of the main component of the blends.

For processing of PLA we have used the 100rpm and set the temperature profile from hopper to die at 160/170/180/180/190. The PHB was processed the screw speed was set to 50 rpm and the temperature profile was 110/130/130/140/140.

The reversed temperature profile of 110/170/160/150/140 was used at 50 rpm for the processing of PBAT and the PCL were process at the same condition as PLA.

The extruder was equipped with a slit die followed by rapid cooling using an air knife. Chill rolls set at ambient temperature were used to stretch the precursor films to obtain 30-35 μm thick films. The precursor films were kept in desiccators (under vacuum) for further characterizations.

All the samples have been dried before processing, to prevent the hydrolysis at elevated temperatures.

3.1.1 Characterizations

a Rheological properties

Rheological characterization of the resins in our study was carried out using parallel-plate geometry on a constant strain rheometer (MCR 301 Anton Paar, Austria). The experiments were performed in the dynamic mode at 190°C for PLA blends under a nitrogen atmosphere and in the frequency range 100 to 0.1 Hz. The up to low frequency setting helps keep the reliable data point before thermal degradation of PLA initiates. A gap of 1 mm under was applied. Prior to frequency sweep tests, time sweep tests were performed at a frequency of 6.28 rad/s for 20 min to check the thermal stability of the samples. In order to avoid the effect of humidity on rheological measurements, all polyester pellets and disk samples were dried in a vacuum oven. The temperature used was 80°C for PLA, PBAT and PHB and 40°C for PCL. Then they were kept in a desiccator.

b Thermal analysis

Differential Scanning Calorimetry (DSC) Q2000 (TA Instruments, New-Castle, DE,

USA) was used for thermal analysis of the resins and films. Three scanning cycles were conducted under nitrogen atmosphere, under heating and cooling rates of 10 °C/min.

At the end of the first heating ramp, the samples were held at 200 °C for 3 min to erase their thermal history before cooling ramp. The melting, crystallinity, and glass transition behavior of the specimens were obtained and discussed.

c Morphology

Scanning electron microscopy (Hitachi S4700 with a cold field emission gun, FEGSEM) was used to observe dispersion quality and morphology of polyester blends. The specimens were impregnated in epoxy resin and microtomed in the MD-ND, MD-TD and ND-TD planes using an Ultracut FC microtome (Leica, Germany) with a diamond knife. The images after composting were taken on the MD-TD plane and also MD-ND planes.

Scanning electron microscopy (SEM) (Hitachi S4700 with a cold field emission gun, FEGSEM) was used to measure the thickness of layers. Part of the films were broken in liquid nitrogen and were coated with gold.

d FTIR analysis

Spectrum 65 FT-IR (Spotlight 400, PerkinElmer) (Waltham, MA) was used to investigate the composition of two phase films and measure the change in the concentration and uniformity of composted samples. The films were analyzed using the ATR setup, MD-TD plane was used and the absorption ratio of specific C=O bonding of each polyester in blends were taken as direct measurement of their concentration.

e Mechanical properties

Tensile tests in both machine direction (MD) were carried out using INSTRON-3365 (USA). Young moduli, tensile toughness, elongation at break and yield strength of the films, were measured according to D 882-02 ASTM standard. Samples with 25 mm width, 10 mm length, and 30-35 μm thicknesses were stretched at a rate of 5 mm/min.

The puncture resistance was evaluated according to ASTM standard D2582 using 250 N load cell of Instron E3000R6454 (USA). The displacement of the film was recorded against the force (N) and the maximum force was reported as the puncture strength. A needle with 0.5 mm radius was used to pierce the film at a rate of 25 mm/min.

f Heat seal measurements

Heat seal experiments were performed on a SL10 LakoTool laboratory hot-tack and seal tester purchased from "Lako Tool & Manufacturing Inc." at a determined temperature, pressure, dwell time and peel rate. Heat seals were made using flat seal bars covered with a layer of Teflon coating. Seal samples were cut in 2.54 cm×33 cm strips specimens parallel to the machine direction and a BOPP tape was used as the back-layer to protect the seal films from fusion and sticking to the hot seal bars. Seal strength experiments were performed based on ASTM F2029 and ASTM F88. T-peel tests were done at a constant peel rate (3.3 mm.s-1) and peel strength was taken as the average plateau peel strength of 5 specimens.

g Composting and disintegration

A laboratory scale composting setup is shown in Figure 3.1-1. The operational parameters involved are temperature (55-65 ºC) and ratio of compost to biodegradable plastic (≈6). Evolved CO_2 can be collected and measured using different techniques, such as gas chromatography and titration. Based on ASTM standard, the titration can be done in saturated solution of $M(OH)_2$, where M is of the metals of second groups. Sample calculation of evolved CO_2 gas using a solution of $Ba(OH)_2$ is determined as is given by (ASTM D5338 2011) which is mentioned in literature review section. The columns are shown in A compost sample was provided by Fafard et Frères, Ltd USA and used for assessing the biodegradability of the film samples.

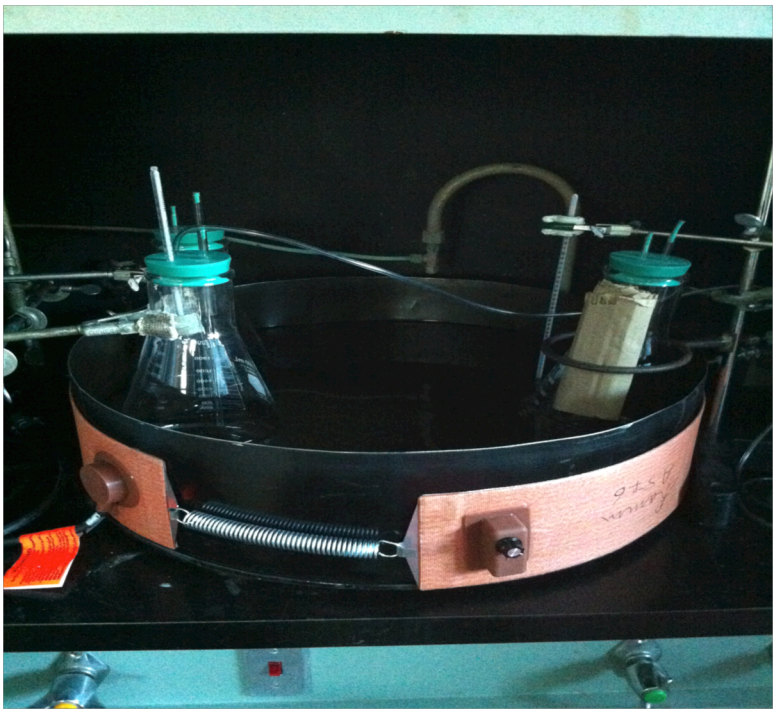


Figure 3.1-1 Composting bioreactors containing Sample, Positive control and Blank vessels.

The biodegradation study was carried out for 40 days. The dimension of the vessels used was 2 liter and it was filled with 600 gr of damp Compost at 70% of its water holding capacity. For the control vessel no film samples were added to the compost. The test vessels were holding an added 100 gr of cut film samples of 5*5 cm^2 size. The initial temperature, relative humidity, and pH of compost were kept constant through the whole biodegradation period. Temperature was monitored throughout the duration of the biodegradation study with a thermometer and a Thermo Haake immersion circulator E52 shown in Figure 3.1-2 was used to control the temperature at around the set point of 55 ºC.

Figure 3.1-2 Thermo Haake immersion circulator E52

After the samples were covered with compost, the vessels were seal with stoppers of two inlets and one outlet for air and water to feed in and CO2 out collections. The samples were also visually inspected, an example is given in chapter 6, and pictures were taken for visual evaluation of its biodegradation to follow the American Standard ASTM 5338.

This system was designed to yield the percentage of carbon dioxide from the organic carbon content of the sample. The compost was sieved through a 5mm sieve.

Figure 3.1-3 Composting vessel , two inlets for water and air and CO_2 outlet set at 55 ℃

Dry compost (600 g) was mixed with 100 g of cut film samples (2.5*2.5) for biodegradability evaluation. For each reactor a blank and positive control (cellulose) were placed in a biodegradation setup.

CHAPTER 4 ORGANIZATION OF ARTICLES

The main achievements of this research are presented in the form of three scientific papers in the following three chapters:

Chapter 4 presents the results of the first paper: "*Development of High Performance Sealable Films based on Biodegradable/Compostable Blends*" published online in the Journal of Industrial Crops and Products. In this work, we investigate the possibility of development of biodegradable blends with superior self-adhesion properties. Thermal and mechanical investigations are performed and the morphological investigation showed that the morphology can be correlated with the seal properties of these blends.

Chapter 5 presents the results of the second paper: "*Tailoring self-adhesion properties of biodegradable polymers through melt blending*" submitted to Journal of applied polymer science. In this work, we study the role of crystallization as a barrier to molecular diffusion and seal formation. Biodegradable blends based on PLA, PCL, and PBAT were investigated for their potential to be sealed at lower temperatures than the melting point of the pure polymers used in their composition.

Chapter 6 presents the results of the third paper: "*Selective Degradation of Biodegradable Blends in Simulated Laboratory Composting*" to be submitted to Polymer degradation and Stability. This paper covers the mechanisms involved in the degradation of biodegradable blends and explored the possibility of selective degradation of each phase of the blends through composting. Combination of ATR-FTIR technique with a composting setup was used to follow the changes in molecular structures.

CHAPTER 5 ARTICLE 1: DEVELOPMENT OF HIGH PERFORMANCE SEALABLE FILMS BASED ON BIODEGRADABLE/COMPOSTABLE BLENDS

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5.1 Abstract

In this study, the seal behavior of toughened blends of Poly(lactic acid) (PLA) and Polycaprolactone (PCL) was investigated in details. The blended samples were prepared using melt blending in a twin-screw extruder and were processed in the form of cast films of about 30μm in thickness. Scanning Electron Microscopy (SEM) study of the morphology of the blends shows that laminar morphology develops in blends of 20% and 40% dispersed phase. Analysis of the thermal behavior of the blends using DSC thermograms reveals significant effect of blending on hindering the crystallization of PCL, resulting in lower crystallinity for samples with high PLA content. Latter provide blends with more amorphous phase and chain mobility, which help lowering the Seal and Hot-tack initiation temperatures. Blending is shown to decrease Seal and Hot-tack initiation temperatures up to 30°C compared to neat PLA. In addition, this technique is proven to be successful to increase the Hot-tack strength of the blends to a comparative level to commercially available seal grade resins at about 1100g/25.4mm for PCL content of 40%. The results indicate that elongation at break increases from about 4% for pure PLA to almost 150% for the blend of 40% PCL and over 400% when PCL content reaches 60%. Higher toughness is an important property for a flexible package and prevents defects caused by its handling and storage conditions.

Keywords: Biodegradable Polymers, Heat Sealing process, Poly(lactic acid) film, Biodegradable blends, PLA toughening.

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[*] Ramin Yousefzadeh Tabasi, Zahra Najarzadeh, Abdellah Ajji, Development of high performance sealable films based on biodegradable/compostable blends, Industrial Crops and Products, Volume 72, 15 October 2015, Pages 206-213, ISSN 0926-

5.2 Introduction

Consumption of significant amounts of polymers in packaging applications has caused many concerns in waste management areas. Although plastics account for about 11% of total municipal waste in United States and Canada, their stability in landfill and their high CO_2 footprint have raised many environmental concerns. (Bohlmann, 2004)On the other hand, many research works have investigated the capability of bio-based and biodegradable plastics to provide promising research area for various applications. (Jiang et al., 2005; Pakravan et al., 2011; Park et al., 2000; Sinclair, 1996)The new approach to replace petroleum based resins with the bio-based and biodegradable materials have given rise to the need for the improvement of the available biodegradable polymers through conveniently inexpensive processes such as melts blending.(Garlotta, 2001; Jiang et al., 2005; Mohanty et al., 2000; Park et al., 2000)

Poly (lactic acid) (PLA) is aliphatic polyester, which shows biodegradable properties and has been the focus of interest of many studies in recent years. In many applications, PLA resin has attracted researchers due to its high tensile strength and modulus. PLA can be a suitable bio-plastic for its ease of processing and temperature range similar to conventional plastics in packaging industry. However, the brittleness of PLA has always been a draw back in many.(Garlotta, 2001; Liu et al., 2010; Nampoothiri et al., 2010; Oyama, 2009; Sinclair, 1996; Theryo et al., 2010) In this work, we are looking for a technique that can make PLA suitable for flexible packaging applications and, specifically, as a seal layer grade material. Considering the thermal and mechanical properties of PLA and the potential of its toughened blends, it is believed that by adjusting the content of modified PLA, a range of flexibility and thermal behaviors can be achieved. The focus on heat-sealing process is because it is an essential step in order to obtain a reliable performance from a flexible multilayer food packaging film structure. (Hashimoto et al., 2006a; Leong et al., 2007; Mazzola et al., 2012; Mueller et al., 1998)

In Seal applications, two interfaces of the same film may come in intimate contact with each other. Then two heated jaws, will heat, press the two films surfaces together and keep them for a given time (dwell time) and in partially molten state till the seal is formed (Hashimoto et al., 2006b; Mazzola et al., 2012; Mueller et al., 1998; Najarzadeh & Ajji, 2014b) Measurement of

Seal and Hot-tack initiation temperatures and the plateau strengths obtained through sealing process are the main aspect of interest in this study.

Likewise any physical process there is a limit to the maximum temperature, minimum time and the maximum plateau strength that can be achieved through heat-sealing process which are dependent of thermal and mechanical and melt behavior of used resins. (Qureshi et al., 2001; Wool, 1995)The Hot-tack strength and Hot-tack initiation temperature are also functions of the above-mentioned behaviors. The main difference is that the strength, one achieves through Hot-tack is mostly related to the melt behavior of the resin, but in seal the solid mechanical behavior plays more significant role. To the knowledge of the writer there are very few works on the investigation of the Hot-tack initiation and strength of the pure and blended resins. (Hashimoto et al., 2006b; Mazzola et al., 2012; Najarzadeh & Ajji, 2014b) Published research works have tried to improve the seal properties of conventional petroleum based resin and existence of detailed study on this behavior for degradable resins is of essential importance. The focus of this work is to show the capabilities of PLA blends to perform as seal layer in packaging in wide range of temperatures and compositions.

5.3 Experimental

5.3.1 Materials

The seal grade polylactic acid (PLA) obtained from Natureworks, Cargill DowLLC. USA, is a copolymer of D&L lactic acid with high D-monomer content and no crystal content (amorphous grade). Also a film grade PLA resin 4032D, from Natureworks as well, has been used for lamination applications. The Poly-ε-caprolactone (PCL) was purchased from Solvay LLC USA. Some of the material's characteristics are listed in Table 5-1 Film sample of pure material as well as their blend in a wide range of concentrations 20% to 80% have been used to cover wide operation window in term of mechanical and seal properties. All the samples have been processed in twin-screw extruder (Leistritz model ZSE 18 HP co-rotating) and were made into films using a cast film die. All the films have been drawn from the melt to a thickness of 30 μm for further analysis.

The temperature profile in the twin-screw extruder along the barrel was set at 170/180/190/190 and the die was set to 190°C. Different blend compositions have been used to prepare the samples. Table 5-2 give the PLA/ PCL ratio in each blend's cast film.

Table 5-1 Melt flow index, density, glass transition temperature and Melting point of PLA and PCL resins.

	MFI g/10 min	Density g/cm^3	Glass transition Temperature	Melting point	Supplier
PLA	12 (190°C-2.16 Kg)	1.27	62	-	Natureworks
PCL	7 (160°C-2.16 Kg)	1.14	-60	60-62	Solvay

Table 5-2 PLA and PCL content used in preparation of sample films through film casting technique

Samples	PLA	80-20	60-40	50-50	40-60	20-80	PCL
PCL Content (%)	0	20	40	50	60	80	100
PLA Content (%)	100	80	60	50	40	20	0

5.3.2 Rheological characterization

Rheological characterization was carried out using parallel-plate geometry by a constant strain rheometer (MCR 301 Anton Paar, Austria). The experiments were performed in the dynamic mode at 190 °C under nitrogen atmosphere in the range of 0.1 to 100 Hz. The viscosity η* and storage modulus G' of the polymers were measured and are shown, as a function of frequency. The time sweep test, show thermal instability of PLA resin after 20min of shearing at 190°C. The frequency sweep test is taking long intervals for measurements at lower frequencies about 0.01Hz, which leads to PLA being sheared for more than said 20min before the instrument measures data at 1Hz and above. This will cause thermal degradation of the less stable PLA resin in measurement time. To obtain more reliable data points, the test was carried out from higher frequencies to lower frequencies. Latter would let us have more accurate data at higher frequencies. (i.e. the higher number of data point will be measured before we reach the limiting time of around 20min explained above.)

5.3.3 Differential Scanning Calorimetery

TA instrument differential scanning calorimeter (DSC) Q 1000 was used to analyze the thermal behavior of the blends. The heating cycle starts from room temperature and the samples were heated to 170 °C at a heating rate of 10 °C/min. the samples were kept at 170 °C to remove previous history then cooled to room temperature afterward at the same rate of 10 °C/min and heated again to 170 °C. The changes in melting point of the blends samples were compared to their neat data and their melting behavior was followed for different composition.

Crystallinity values, reported in the graphs, are calculated using a heat of fusion of 136 J/g for fully crystalline Poly[ε]-caprolactone.(Guo & Groeninckx, 2001)

5.3.4 Scanning Electron Microscopy (SEM)

The blends samples were molded in epoxy resin then microtomed using an ultra-microtome equipped with a diamond knife at -100°C and then coated with platinum vapor. The films were Cryo- microtomed in both Machine Direction (MD) and transverse (TD) directions. A high resolution Hitachi S-4700 microscope operated at 2 kV accelerating voltage was employed for FEG-SEM.

5.3.5 Thermal Lamination

To prepare samples for the Seal and Hot-tack experiments, all the samples needed to be protected by a film layer of higher melting material than that of the experimental temperature window. The film chosen for this application was semi-crystalline PLA film, which has a melting point of 168°C, higher than the maximum sealing temperature of 115°C. The lamination was carried out using Lab scale thermal laminator (BJ Creation Inc.).

5.3.6 Mechanical Tests

Tensile test were performed to determine the mechanical behavior of the blends. Testing was carried out in accordance to the ASTM D882 on an Instron (Norwood, MA) 3365 universal testing machine with a 500 N load cell. The Young modulus, stress and strain at yield, and stress at break were measured. In order to determine mechanical properties, a crosshead speed of 12.5 mm/min was used.

5.3.7 Seal and Hot-tack

Lab scale SL100 Lako-Tool instrument was utilized to investigate seal and Hot-tack behavior of the prepared samples. The tests were performed under specifications mentioned in

the ASTM F88 and F2029 experimental methods. Metallic jaws covered by Teflon were used and the sealed area was 19.1mm×25.4mm on sample strips 25.4mm width×330.2mm length. An average over at least five experiments for each sample was used for each specific temperature. The pressure was set to 0.5 N/mm^2 and the dwell time fixed for all samples at 1s. These conditions will allow us to measure the seal properties more precisely for PLA resin, which is not forming very strong bonding through sealing at low dwell times.

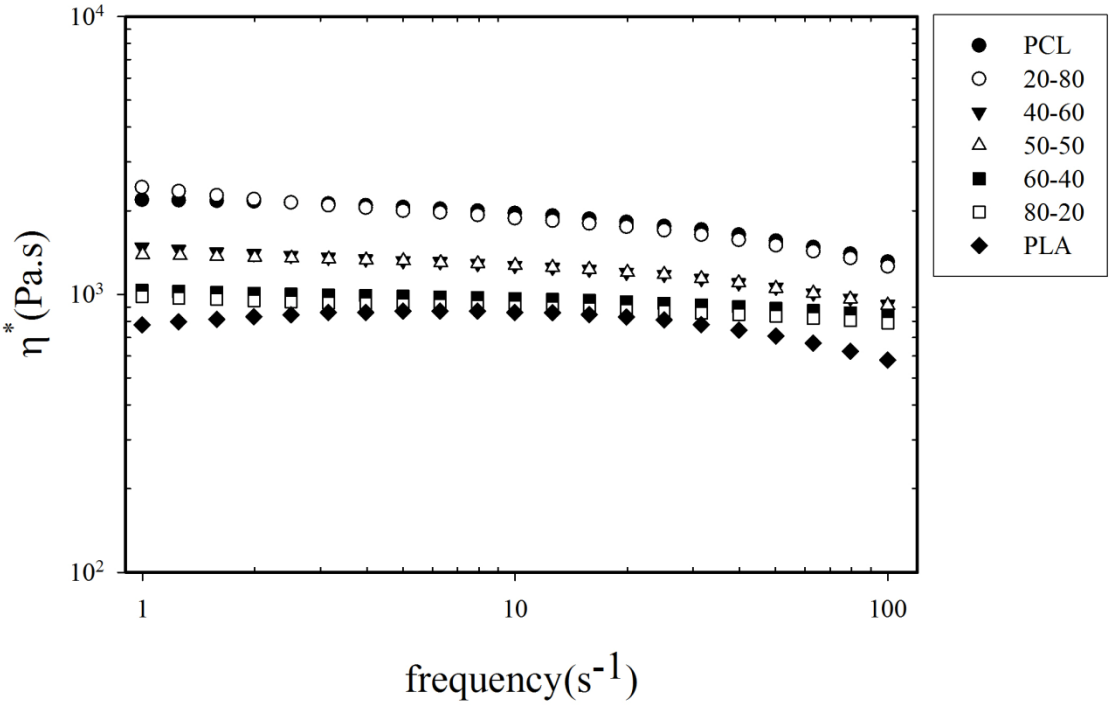
5.4 Results and discussions

5.4.1 Viscoelastic behavior analysis

Blending of two thermoplastic resins is directly influenced by, their melt viscosities and viscosity ratio ($\lambda=\eta_d/\eta_m$) as well as their interfacial interactions. In blends of Poly (lactic acid) and Polycaprolactone, likewise an immiscible blend, final blend properties depend on the morphology of the blend. The final morphology of blend, as will be explained in morphology section, is indivisible of their melt rheology and interfacial tension. The melt shear viscosity of PLA and PCL was measured at 190°C and is illustrated in Figure 5.4-1. Due to PLA thermal degradation, the data below 0.1 Hz are not reported in the graphs. In this study, viscosity ratio coupled with low interfacial tension of the components (Sarazin et al., 2004), as we will see, led to the formation of laminar morphology in the blend systems.(Gonzalez-Nunez et al., 1993; Kamal et al., 1995) An increase in viscosity ratio to about 2.4 will develop long fibrils, which has been shown in the work of Kim et al and Gonzalez-Nunez et al. (Gonzalez-Nunez et al., 1993; Lee & Kim, 1997) Figure1a indicates that for actual process shear rates (about 30-50 s^{-1} in cast die and 200-300 s^{-1} in the extruder); the viscosity ratio of the melts in the die is about 2.3, with the PCL having higher viscosity. In addition, elongational flow in the coat hanger die will force the disperse phase to elongate in the transverse direction, which mean that the elongated fibrils in the MD would also elongate in TD to form elongated ovals dispersed inside the films.(Ajji & Utracki, 1996; Gonzalez-Nunez et al., 1993) In this study we will address this type of morphology as laminar morphology.

Figure 5.4-1b present the storage modulus of the blends. The non-terminal behavior at low frequencies in the storage modulus of the blends is related to the shape relaxation of dispersed phase. (Bousmina et al., 1995; Maani et al., 2011) Through relaxation process, total area of the interface is changing. This change in the area would affect the interfacial energy and also the contribution of interfacial energy to the storage modulus consequently. At high

frequencies, this effect would become negligible, as the energy of deformation of each phase would increase significantly.



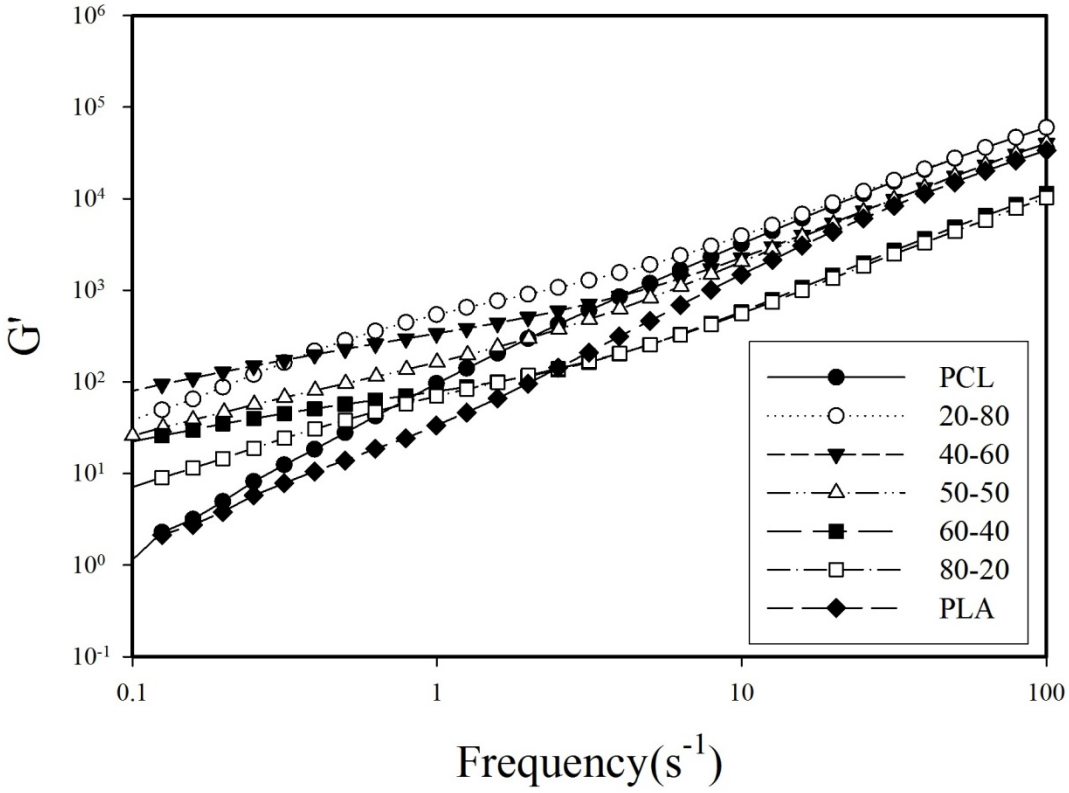


Figure 5.4-1 1a and 1b show the complex viscosity (η) and storage modulus (G') of the pure and blended resins respectively*

5.4.2 Thermal Characterization

Film samples have been analyzed using differential scanning calorimetry to investigate the thermal behavior of the prepared blends. The DSC results are shown in Figure 5.4-2. The endothermic peak around 60°C is associated with the melting point of PCL resin. (Newman et al., 2009) The addition of PLA to PCL samples will form a separate PLA domains and act as nucleating agent, this phenomena is acting in competition with the hindering effect caused by lower movement of PLA molecular chains which on the other hand retard the formation of PCL crystals and lowers the crystallinity of blend samples which, will cause an increase in the enthalpy of fusion of samples, Figure 5.4-2, followed by a decrease in crystallinity at higher concentrations of PLA above 60%.

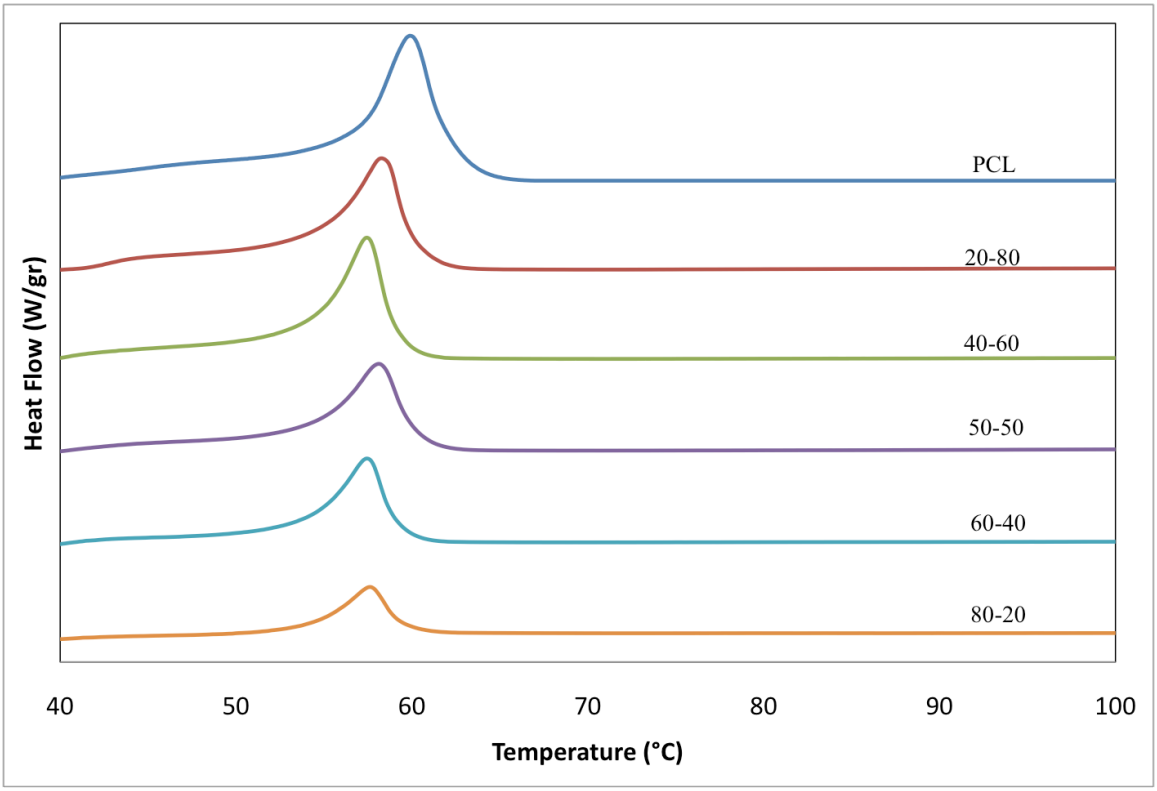


Figure 5.4-2 The DSC thermogram of blend samples. The Melting peak of PCL is noticeable at around 60°C

The normalized enthalpy of melting of PCL in the blends, obtained from DSC results, is shown in Figure 5.4-3 and was used to determine the crystal content of the blends. Latter is one of the affecting factors, which change the seal initiation temperatures as will be discussed later. As indicated in Figure 5.4-3, in the third cycle, blends with low concentration of PLA, lower than 80%, have higher crystallinity than pure PCL. This may occur due to the participation of solidified PLA particles, as nucleating agent, at the crystallization temperature of PCL at around 30-40 °C as explained above. Therefore the crystal content of PCL in the blends increase to a maximum content of around 40% for PLA concentration of 40%, which is illustrated in Figure 5.4-3. In blend samples containing higher PLA concentrations than 40%, the rigid PLA chains would decrease the chain mobility of PCL molecules gradually and hence lower the crystalline content of PCL in blends. The same trend in blends of PLA and PCL has been observed in the work of Newman et al. (Newman et al., 2009) They reported their results for blends of the same range of concentrations using different detection methods. The results they obtained are in agreement with our results.

The crystallinity can be a significant barrier to molecular inter-diffusion at the surface of the films. This will suggest that the observed decrease in the crystal content of the PCL dispersed phase would increase the mobility of rubbery polymer chains at the seal temperature, which will lead to significant decrease in seal initiation temperature of pure PLA by addition of PCL which, will be addressed later.

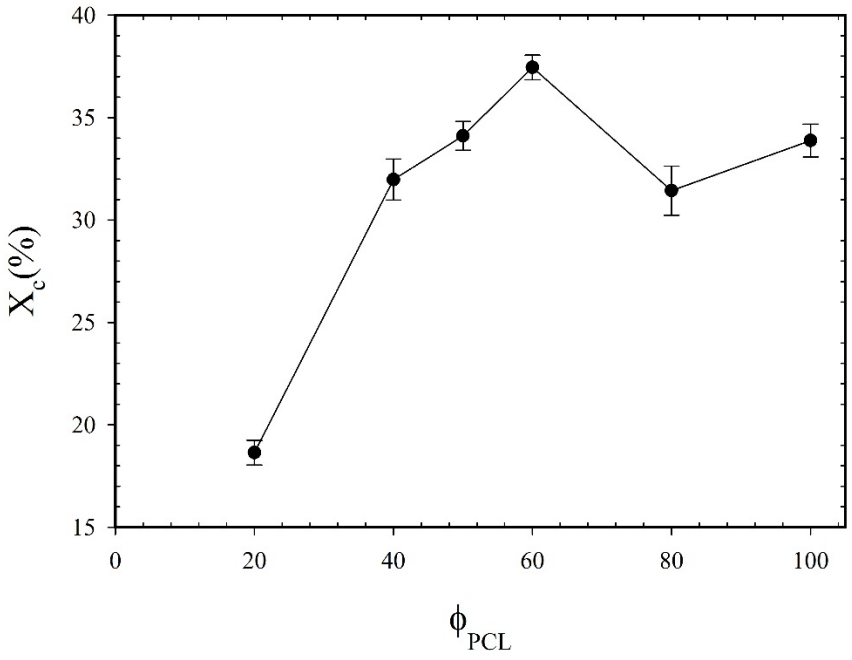


Figure 5.4-3 Crystallinity of pure and blend samples obtained from normalized enthalpy of melting of the blends

5.4.3 Morphology development

Morphology of polymer blends is highly affected by their viscosity and viscosity ratio as well as their interfacial tension and thermodynamics as well as stress fields before solidification. (Utracki & Shi, 1992) Some researchers have shown that the interfacial tension of PLA and PCL is very low due to the same chemical bonding and chain structure of these two resins. In other words, there is no need for the use of a compatibilizer to obtain good final mechanical properties

(Ajji & Utracki, 1996; Sarazin et al., 2004; Semba et al., 2006; Takayama et al., 2006) And from our calculations from the surface tension of these two polymers (50mN/m for PLA($\gamma^d = 37, \gamma^p = 13$) and 52 mN/m for PCL($\gamma^d = 41, \gamma^p = 11$) using harmonic mean equation the interfacial tension of two polymers is calculated to be 0.37 mN/m. (Wu, 1973)

In film casting process, the film will be cooled down to room temperature in few seconds by means of forced airflow over the film surfaces and chilled rolls. This type of process would not allow the developed morphology to relax and form thermodynamically stable morphology that we would expect from the annealed blends, which have been prepared in internal mixers and cooled over long times. (Favis & Chalifoux, 1988; Lepers et al., 1999; Willis et al., 1991)

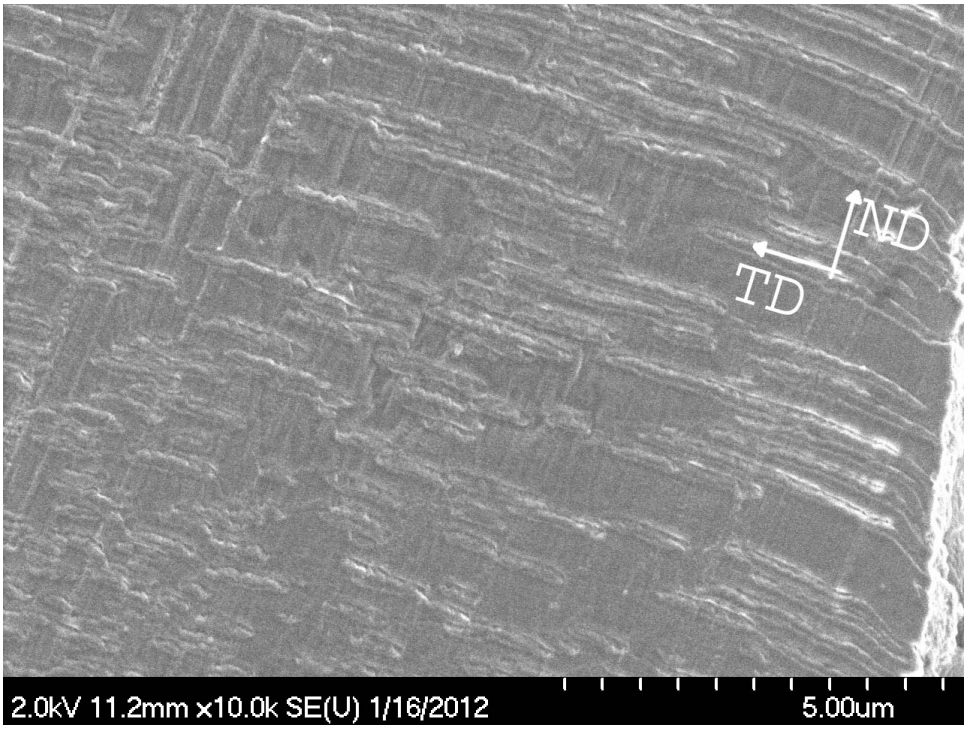
As discussed before, the same polyester bonds in PLA and PCL would allow a good interaction between the dispersed phase and the matrix and favor the formation of stretched droplets, fibrils and laminar morphology in elongational flow in cast film die. In terms of the viscosity of the blends, as shown in Figure 5.4-1, both PLA and PCL have the same order of magnitude of viscosity at the processing temperature of 190°C, which will facilitates stress transfer from matrix to disperse phase and increases the chances for laminar morphology development. Figure 5.4-4 shows the developed morphologies through the film casting of PLA and PCL blend for blends containing 20% and 40% of dispersed phase. The SEM micrographs show clearly the elongated morphology in the films. An increase in PCL content leads to larger dispersed domains. Phase inversion is correlated to the viscosity ratio of the phases in the blends so that the melt viscosity of each component (η_i) and their critical phase inversion content (φ_i) are inversely related as implied by brown (Sarazin et al., 2004) equation:

$$\frac{\varphi_1}{\varphi_2} = \frac{\eta_1}{\eta_2} \qquad eq.4.4-1$$

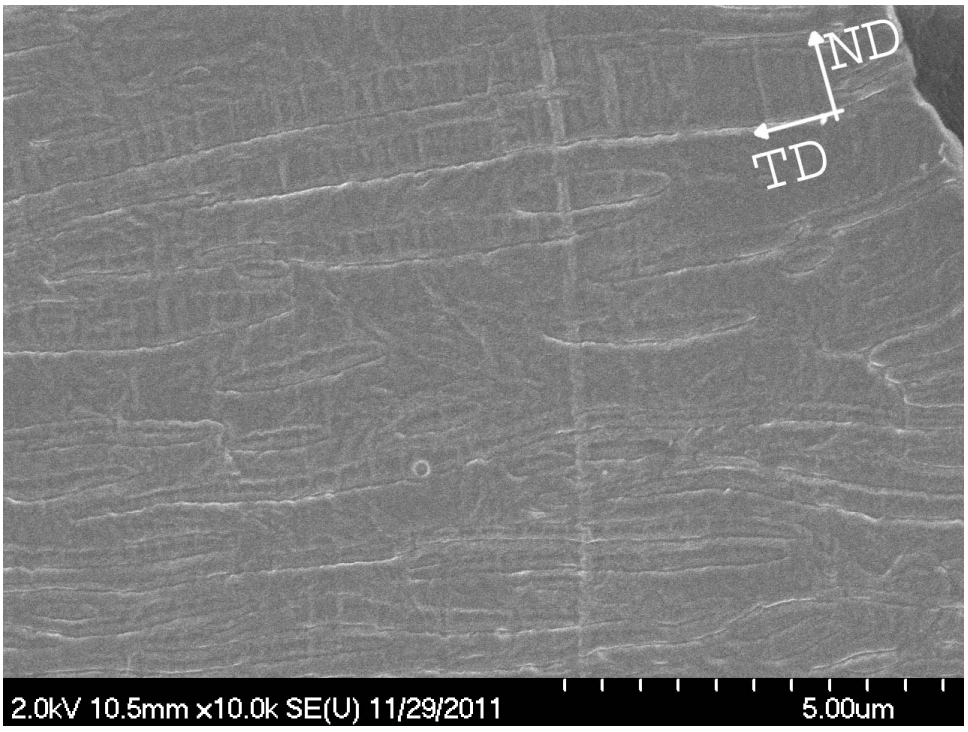
Phase inversion for PLA/PCL blends is expected to happen at PCL contents between 40%-60%. (Gonzalez-Nunez et al., 1993; Sarazin et al., 2004; Semba et al., 2006) Almost the same morphology was observed in the blends of 60% and 80% PCL as continuous phase (graphs are not presented). This type of elongated morphology would provide large aspect ratio of dispersed phase. The higher aspect ratio will increase the chances of stronger bonding at lower temperature through diffusion of dispersed phase at the films interfaces. In other words, the seal initiation temperature would decrease as the larger fraction of surface is covered by PCL elongated particles. As expected the extent of elongation in machine direction is greater than

transverse direction, Figure 5.4-4, which shows the effectiveness of melt drawing through cast film processing in deformation of dispersed phase to form a laminar structure.

As the concentration of PCL increases and the phase inversion happens; a significant threshold in the seal properties was detected, Figures 7, which relates to the higher mobility and diffusion of PCL as continuous matrix.



(a)


ND
TD
2.0kV 10.5mm x10.0k SE(U) 11/29/2011
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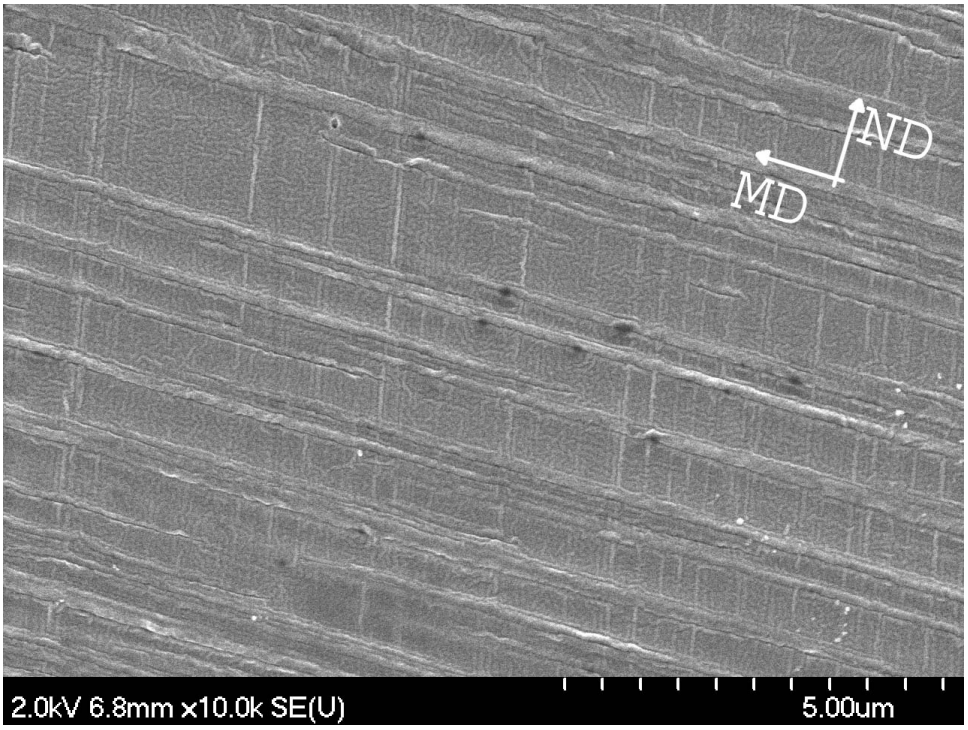
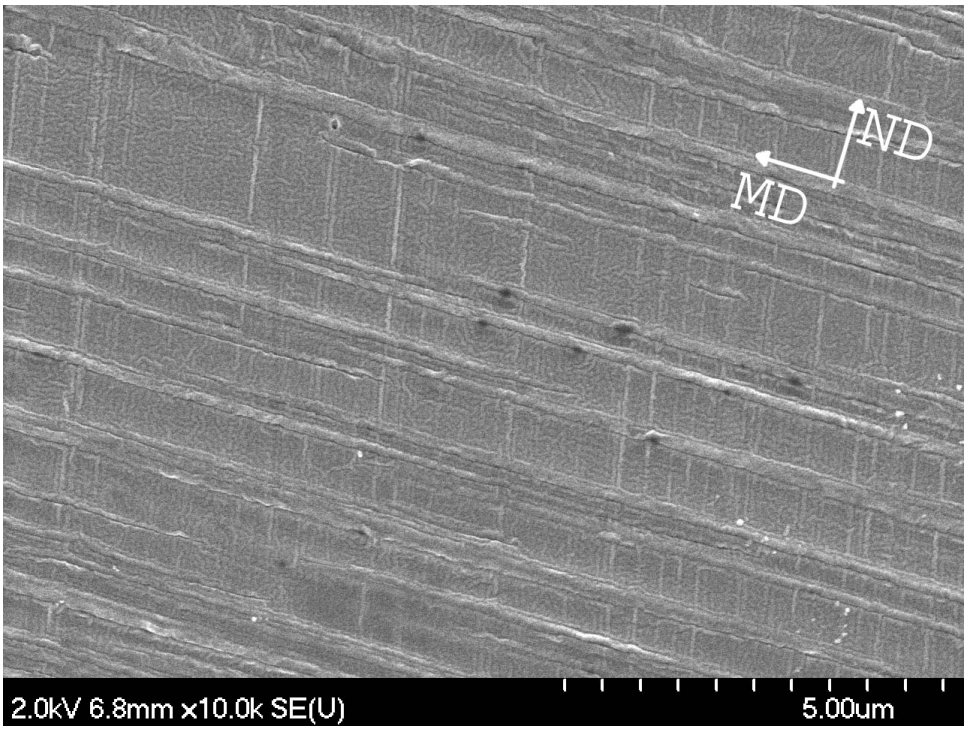
(b)


ND
MD
2.0kV 6.8mm x10.0k SE(U)
5.00um

(c)



(d)

Figure 5.4-4 SEM micrographs of film samples showing laminar morphology for sample with 20% PCL microtomed perpendicular to machine direction (MD) (a), sample with 20% PCL microtomed perpendicular to transverse direction (TD)(b) and 40% PCL; microtomed perpendicular

5.4.4 Mechanical properties

PLA as a bio-based material has high tensile strength and high modulus comparable to PET and nylons. These properties appeal to many granted studies to find applications, where PLA can replace conventional petroleum based resins. But there is a drawback, as the PLA brittleness and low elongation at break limits its use in many applications.

Many researchers have addressed the capability of several rubbery polymers to help toughening the PLA resin. (Liu et al., 2010; Nampoothiri et al., 2010) Among the methods to improve the toughness of PLA, melt blending is more cost effective and applicable. (Anderson et al., 2008; Semba et al., 2006) PCL is one of the proven materials, which could help toughen PLA in blends. (Anderson et al., 2008; Liu et al., 2010; Oyama, 2009; Semba et al., 2006; Theryo et al., 2010) Cast films from blends of PLA and PCL showed significant improvement in elongation at break, at PCL concentrations of about 20% and above, while Young's modulus remained at an

acceptable range for packaging application. Figure 5.4-5 shows pure resins and blends tensile behavior.

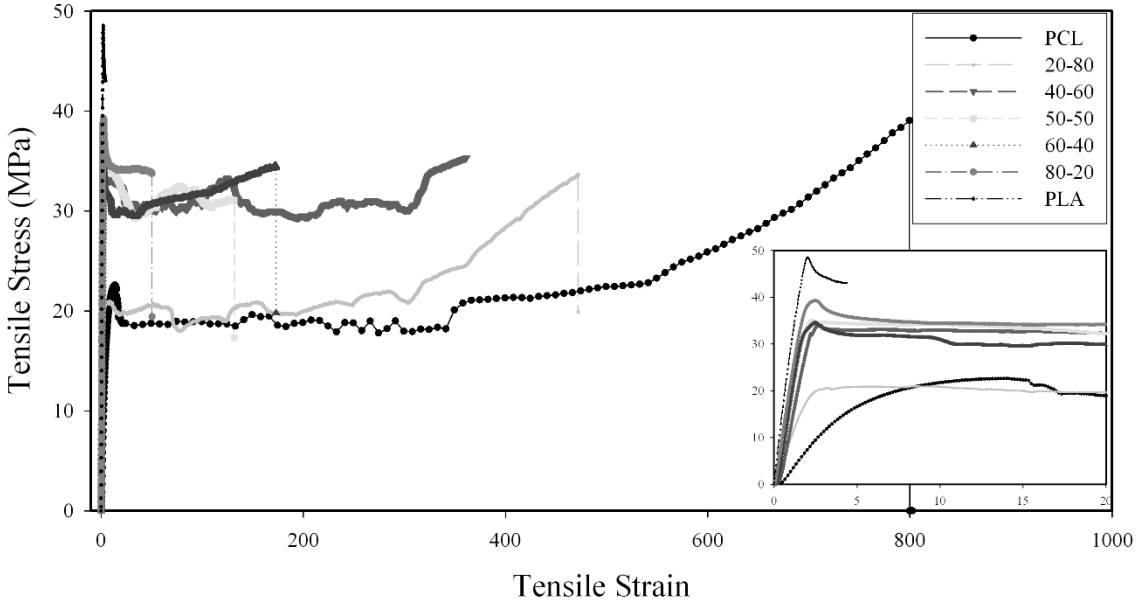


Figure 5.4-5. Blends stress-strain graphs showing significant increase in elongation at break and gradual decrease in tensile modulus

Increasing PCL content in the blends increased significantly the elongation at break (from about 4% for pure PLA to about 500% for 80% PCL) while the modulus and tensile strength decrease gradually. Figure 5.4-6 shows the variation in the Young's modulus of the blends as a function of PCL content. The straight line shows the expected results for modulus from the mixtures rule calculations. As discussed the same polar bonding between two resins help maintain the modulus close to mixtures rule prediction, which is the ideal prediction for the materials with very close chemical structure and molecular interactions. But by increasing the PLA content over 20% the blend would show deviation from mixture rule. Figure 5.4-3 as discussed gives an idea of change in the crystallinity of PCL content. As the PLA content increases the crystallinity of the PCL increase to a maximum and then decrease gradually this type of behavior has been also reported for PET/PP blends by Bataille et al. (Bataille et al., 1987) The gradual positive deviation of Modulus can be attributed to the said change in the crystallinity of PCL phase and as the crystallinity decrease the modulus lowers to the mixtures rule prediction, which is shown by solid straight line. Many research works have tried to predict the modulus of blend using the neat polymer properties and carrying out theoretical calculations. The known

models are Mixtures rule model, Foam model and two variations of Kerner–Uemura–Takayanagi model (KUT model with perfect adhesion between the dispersed phase and matrix and with no adhesion)(Simões et al., 2009). These entire models expect no effect of one phase on the other one and the predicted modulus is always lower than the rule of mixtures.

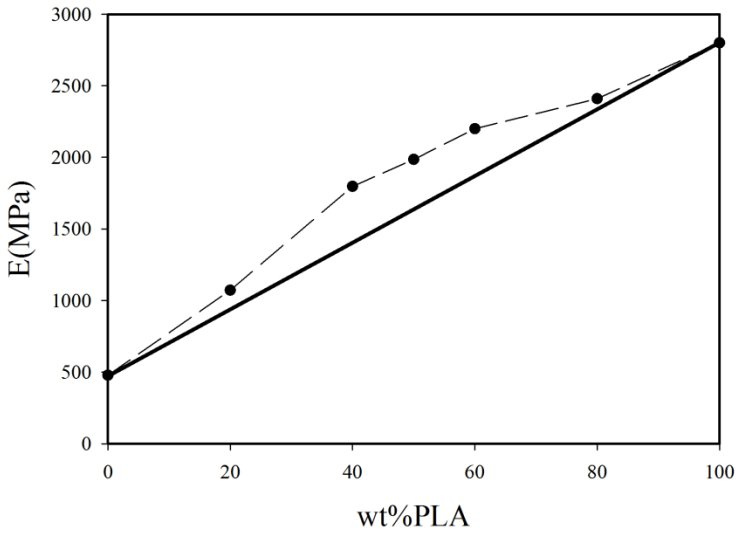


Figure 5.4-6 Young's modulus of blends vs. the PCL content, the straight line is mixture rule prediction

5.4.5 Seal and Hot-tack properties

To study the seal performance of the blends films, seal and Hot-tack experiments were performed in a wide range of temperatures. Performing seal experiments in different temperatures for each composition results in an individual curve for each sample. In order to verify how a seal layer performs, a combination of seal and Hot-tack initiation temperatures as well as its plateau seal strength and Hot-tack strength should be measured.

The Hot-tack curves for PLA/PCL blends are presented in Figure 5.4-7. From the curves, the Hot-tack plateau strength for pure PLA is about 800 (g/25.4mm) and increases gradually with incorporation of PCL.

Hot-tack initiation temperature shows a decrease of 15°C by addition of 20% PCL and an additional 10°C at 40% PCL as illustrated in Figure 5.4-7. Incorporation of linear PCL chains, into PLA matrix, improves chain mobility and diffusion of blends. Higher diffusion results in stronger bonding at the films interfaces at lower temperatures. In addition, increased Hot-tack

strength at lower temperature can be attributed in part to the higher aspect ratio of the dispersed phase discussed in Figure 5.4-4.

Although a sharp decrease in initiation temperature at low PCL content blends was observed, this slope decreased when PCL content exceeded 50% and the samples showed gradual decreases in Hot-tack initiation temperature. Figure 5.4-7 presents Hot-tack data showing a decrease in the Hot-tack initiation temperature as well as an increase in Hot-tack strength by addition of PCL in the blend.

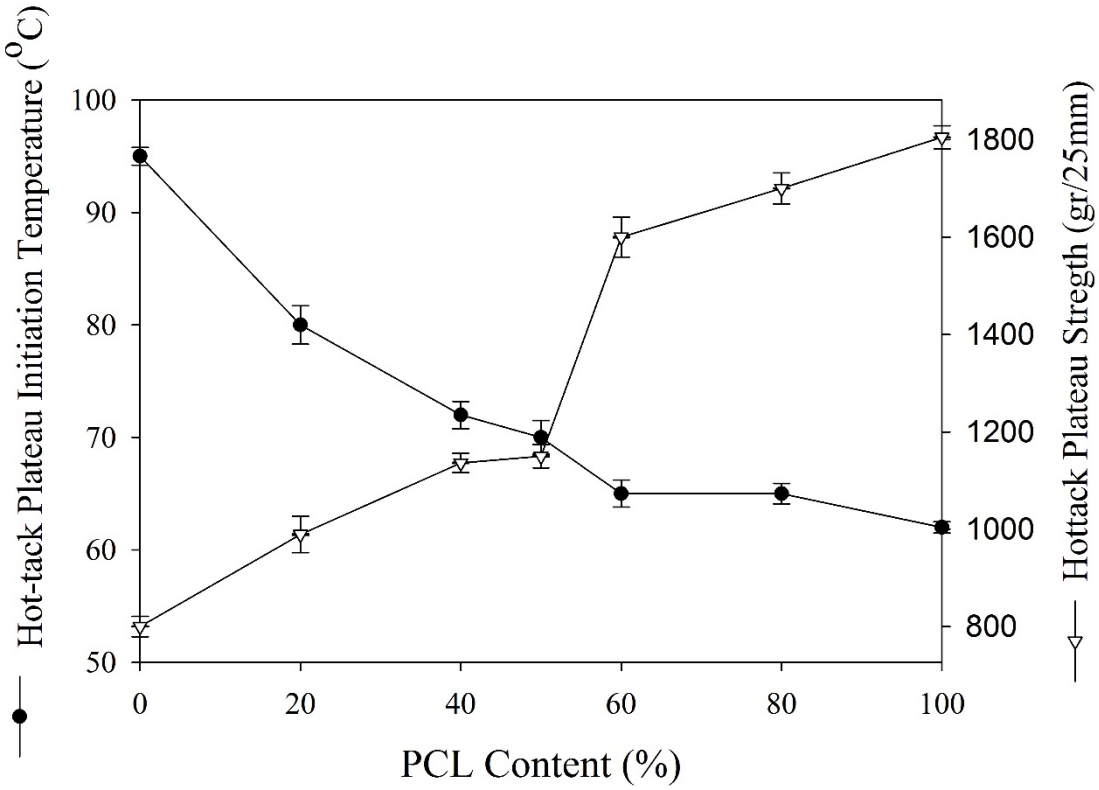


Figure 5.4-7 Hot-tack data showing the decrease in the Hot-tack plateau initiation temperature as well as the increase in Hot-tack strength by the addition of PCL in the blend

The Hot-tack strength increases by addition of 80% PCL to almost twice as much as the Hot-tack strength of pure PLA. This increase as discussed results from higher chain mobility of blends and thus higher diffusion in the films interfaces. This range of Hot-tack is comparable to commercially available polyethylene based seal grade resins.

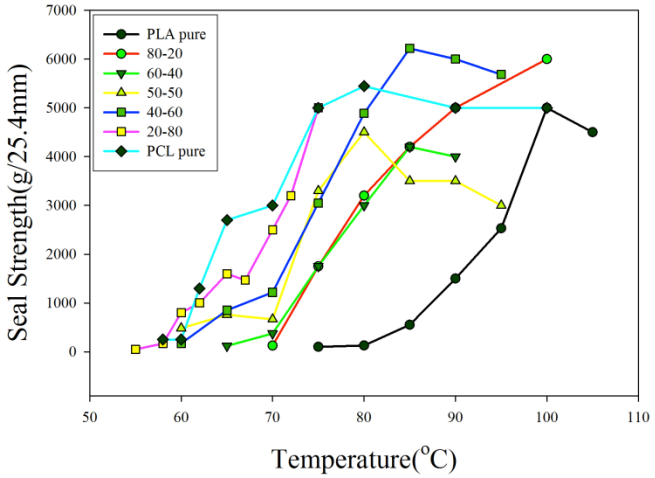


Figure 5.4-8 Presents seal data vs. different PCL contents indicating the decrease in the seal initiation temperature by the addition of PCL in the blend

Lower seal initiation temperature is also observed by addition of PCL to PLA through melt blending. Figure 8 shows the significant effect of blending on lowering the seal initiation temperature. The strong seal strength in PLA and blends is mostly due to the high polarity of their repeating group. The polar chemical bonds coming from the nature of polyesters' heteroatomic bonds will give rise to very strong intermolecular interactions between polymer chains.

5.5 Conclusion

Blending is a promising technique to enhance the mechanical and seal properties of PLA. Addition of PCL enhanced seal behavior of PLA film both in term of the decrease in seal and Hot-tack initiation temperatures and increase in Hot-tack strength. Addition of 20% PCL led to an elongation at break of up to 150% and higher seal strength, which mean more flexible seal layer with improved seal properties.

Higher Aspect ratio of dispersed phase obtained at high PCL contents, provided more film surface of higher diffusivity during the seal process, leading to higher Hot-tack strength and lower Hot-tack and seal initiation temperatures. Blending of PCL with PLA led to the improvement of PLA brittleness.

5.6 Aknowledgement

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CHAPTER 6 ARTICLE 2: TAILORING SELF-ADHESION PROPERTIES OF BIODEGRADABLE POLYMERS THROUGH MELT BLENDING

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6.1 Abstract

In this study, we address the effect of blending on self-adhesion properties of poly (lactic acid) (PLA) and its blends with Poly (butylene adipate-*co*-terephthalate)(PBAT). The objective is to develop a correlation between blends crystalline structure and morphology and the corresponding self-adhesion of films thereof. PLA resin is blended with PBAT and film samples were prepared from both pure resins and the blends using film casting technique. Film surfaces were put in intimate contact for 1s at the pressure of 0.5Nmm^{-2} and in the temperature range of 70°C to 140°C to measure the adhesion related properties. To distinguish the effect of crystallization, both amorphous and crystalline PBAT films have been tested and compared to their blend with PLA. The thermal analysis shows a significant effect of crystalline structure of PBAT on shifting its self-adhesion initiation temperature (T_{si}) up to 20°C. Incorporation of PBAT as a dispersed phase also shifts (T_{si}) of blend samples. The gradual decrease in PBAT crystallinity in the blends caused by the hindering effect of PLA rigid molecules correlates with the shift in their self-adhesion initiation temperature. The SEM micrographs show the two phase elongated morphology where stretched ellipsoids developed through elongational flow during the cast film process. This morphology represent higher aspect ratio of the dispersed phase which enhances the adhesion process. The blends also show higher toughness and better puncture resistance as a result of blending, which is an asset for flexible packaging applications and would guarantee the performance of the seal layer.

[†] Ramin Yousefzadeh Tabasi, Abdellah Ajji, *Tailoring self-adhesion properties of biodegradable polymers through melt blending* Submitted to Journal of applied polymer science

6.2 Introduction

Recent developments in the production of polymeric articles from plastics, which are capable of undergoing microbial degradation has opened up chances to replace many conventional petroleum based plastics with their bio-based and biodegradable counterparts.(Anderson et al., 2008; Bohlmann, 2004; Garlotta, 2001; Najarzadeh et al., 2014; Oyama, 2009; Sarazin et al., 2004) Packaging industry, specifically food packaging industry, sees its own opportunity to take advantage of these new advances.(Garlotta, 2001; Najarzadeh et al., 2014; Nampoothiri et al., 2010; Park et al., 2000; Sarazin et al., 2004; Sinclair, 1996; Wehrenberg, 1981)

Non degradable polymeric films, due to their relatively high specific surface area, represent a potential danger to the environment because of their resistance to degradation by living organism, choking the soil, reflecting sun rays etc.(Avella et al., 2005; Gindl & Keckes, 2007; Gross & Kalra, 2002; Siracusa et al., 2008) Recycling, which is considered as one of the means of resolving pollution problems, loses its efficiency in food packaging.(Gross & Kalra, 2002; Siracusa et al., 2008) Food contamination, presence of a variety of materials (such as in multilayer structures), cost issues and loss of mechanical properties are among the restricting factors limiting polymers to be recycled.(Siracusa et al., 2008) These issues lead to more eagerness of industry to find a solution to eliminate the post-use polymeric film dangers. Application of biodegradable and compostable plastics has been proven to be an effective approach to this matter.(Garlotta, 2001; Gross & Kalra, 2002; Najarzadeh et al., 2014; Nampoothiri et al., 2010; Park et al., 2000; Sarazin et al., 2004; Sinclair, 1996; Siracusa et al., 2008; Wehrenberg, 1981) However, beside the benefits these bio-based and biodegradable resins provide, there are many processing and application challenges that are to be solved by applying engineering techniques, such as copolymerization, blending and development of multilayer structures in order to achieve the desired performances.(Anderson et al., 2008; Nampoothiri et al., 2010; Platt & Limited, 2006; Sinclair, 1996; Siracusa et al., 2008)

In a food package, protection of food from external contaminations, oxidation, as well as odor loss are of outmost importance. (Fereydoon et al., 2014; Najarzadeh & Ajji, 2014b; Nampoothiri et al., 2010; Wagner, 2009)

What guarantees the barrier feature of packages is the capability of the seal layer in their structure, to provide flawless hermetic seal. Latter is often made possible by use of a plastic layer,

which is designed to self-adhere at a convenient processing condition. Even in the case of conventional petroleum based polymers, only few works address the self-adhesion in practical conditions. This becomes more problematic for biodegradable and bio-based materials as even fewer literature addressed their sealability performances.(Najarzadeh & Ajji, 2014b; Najarzadeh et al., 2014; Platt & Limited, 2006)

A convenient method to investigate the self-adhesion of glassy and semi-crystalline polymer is to keep the analogous surfaces of pure or blended polymer article in an intimate contact at certain temperature and pressure for a defined period of time. Said process may be referred to as Welding, Sealing, Hot-tack or Crack healing process.(ASTM F1921 / F1921M-12e1 2012; de Gennes, 1983; de Gennes, 1971; Wool & O'connor, 1981; Wool et al., 1989; Wool, 1995)

Joining process can be described based on the reptation theory, considering the diffusion of polymeric chains through their tube to the adjacent surface of the same composition.(de Gennes, 1983; De Gennes, 1990; de Gennes, 1971) This molecular approach requires a complicated set of calculations, which have mostly been done for ideal conditions for pure material and long processing time as well as fixed operating temperature.(Basin, 1967; Schnell et al., 1998; Stamm et al., 1991; Wool et al., 1989) In practice, this method of calculation is essentially impossible for blends with a matrix and dispersed phase morphology, which are non-isotropic in nature and are self-adhered in hot-tack processes at short times and non-isothermal conditions. (Najarzadeh & Ajji, 2014b; Voyutskii et al., 1966; Zhao et al., 1993)

A macroscopic approach using correlations between the material behavior and its physical and chemical characteristic is more suitable in this matter. Prud'homme et al (Boiko et al., 2001) studied the effect of elimination of crystal structure on the shift of sealing temperature of poly(ethylene terephthalate)(PET). They have based their experiment on the theory given by Mayes et al (Mayes, 1994) and also Kajiyama et al (Kajiyama et al., 1995) implying that the surface of amorphous polymers have a lower Tg than the bulk material. Prud'homme et al. (Boiko et al., 2001; Boiko & Prud'homme, 1999; Boiko & Prud'homme, 1998) performed a series of experiment on different polymers and have shown the possibility of joining polymeric material below their bulk Tg. Development of amorphous materials for self-adhesion applications has been noticeably on the rise, as many companies provide amorphous grades for seal layers

applications. The greatest issue with the application of these amorphous resins, which are usually copolymers, is their processability and in case of PLA also its undesirable brittleness.

A customary method to make amorphous polymeric article from a semi-crystalline polymer is fast cooling from the melt (quenching), which can be done by means of immersing the molten polymer into liquid nitrogen. This method has shown to be effective in the case of PET, resulting in surface healing temperatures of up to 17ºC below its Tg. (Boiko et al., 2001)

Laredo et al. (Newman et al., 2009) have shown the gradual decrease in crystallinity of Poly-ε-caprolactone in blends with PLA as the content of PLA reaches above 40% which has also been confirmed by a previous work done in our group (Tabasi et al., 2015) The same approach can be followed to lower the crystallinity of semi-crystalline aromatic copolyesters such as PBAT to lower their crystallinity and hence their seal initiation temperature (T_{si}). To our knowledge few works have addressed the self-adhesion in biodegradable plastics and there is a need for further investigation of the self-adhesion of biodegradable blends. In this study we will investigate the effect of blending on controlling the crystallinity and self-adhesion behavior of biodegradable resins and we aim to show the capability of tailored biodegradable blends to be used in packaging application and perform comparative to commercial petroleum based resins.

6.3 Experimental

6.3.1 Materials and processing

The amorphous polylactic acid (PLA) 4060D was obtained from Natureworks, USA. The Poly(butylene adipate-*co*-terephthalate) (PBAT) was provided as commercial grade Ecoflex FBlend C1200 by BASF, USA. Table 6-3 gives some of the physical properties of the pure resins. Film samples of blends at different concentrations from 5% to 40% were used to measure the mechanical and self-adhesion properties. Cast film technique was used to prepare the film after melt mixing in twin-screw extruder (Leistritz model ZSE 18 HP co-rotating) at screw speed of 100RPM with barrier zones set at 165 ºC/175 ºC/175 ºC/180 ºC and die set to 160 ºC to adjust the melt strength. Films thicknesses were adjusted to reach 35µm. Table 6-2 give the PLA/ PBAT ratio in blends.

Table 6-1 Melt flow index, density and Melting point of PLA and PBAT resins.

	Melt Flow index (g/10min)	Density ($g/cm^{3)}$	Melting point (°C)	Supplier
PLA	8-12 (190°C-2.16 Kg)	1.27*	-	Natureworks
PBAT	2.7-4.9 (160°C-2.16 Kg)	1.25-1.27*	110-130	BASF

Table 6-2 . PLA/PBAT concentration in blends.

Samples	PLA	PLPB95-5	PLPB90-10	PLPB80-20	PLPB60-40	PBAT
PBAT Content (%)	0	5	10	20	40	100
PLA Content (%)	100	95	90	80	60	0

6.3.2 Differential Scanning Calorimetry

In order to analyze the thermal behavior of the blends, we used TA instrument differential scanning calorimeter (DSC) Q 1000. Standard heating rate of 10ºC was used for three cycles of heating, cooling and heating in the temperature range of -30 to 180 ºC. This grade of PLA is completely amorphous and show no melting peak. The recorded heat of melting is taken as heat of melting of PBAT and have been compared to pure PBAT samples to measure the crystalline content of resins. Crystallinity values, reported in the graphs, are calculated using a heat of fusion of 114 J/g for fully crystalline Poly(butylene adipate-*co*-terephthalate)(Al-Itry et al., 2012). To investigate the effect of thermal treatment on the crystallinity of Poly(butylene adipate-*co*-terephthalate), its film samples have been made in two series. First the films were analyzed using DSC instrument to determine their crystal content as presented in Figure 6.3-1. We have then thermally treated the film samples to remove the crystalline structure at 170 ºC and then quenched them in liquid nitrogen.

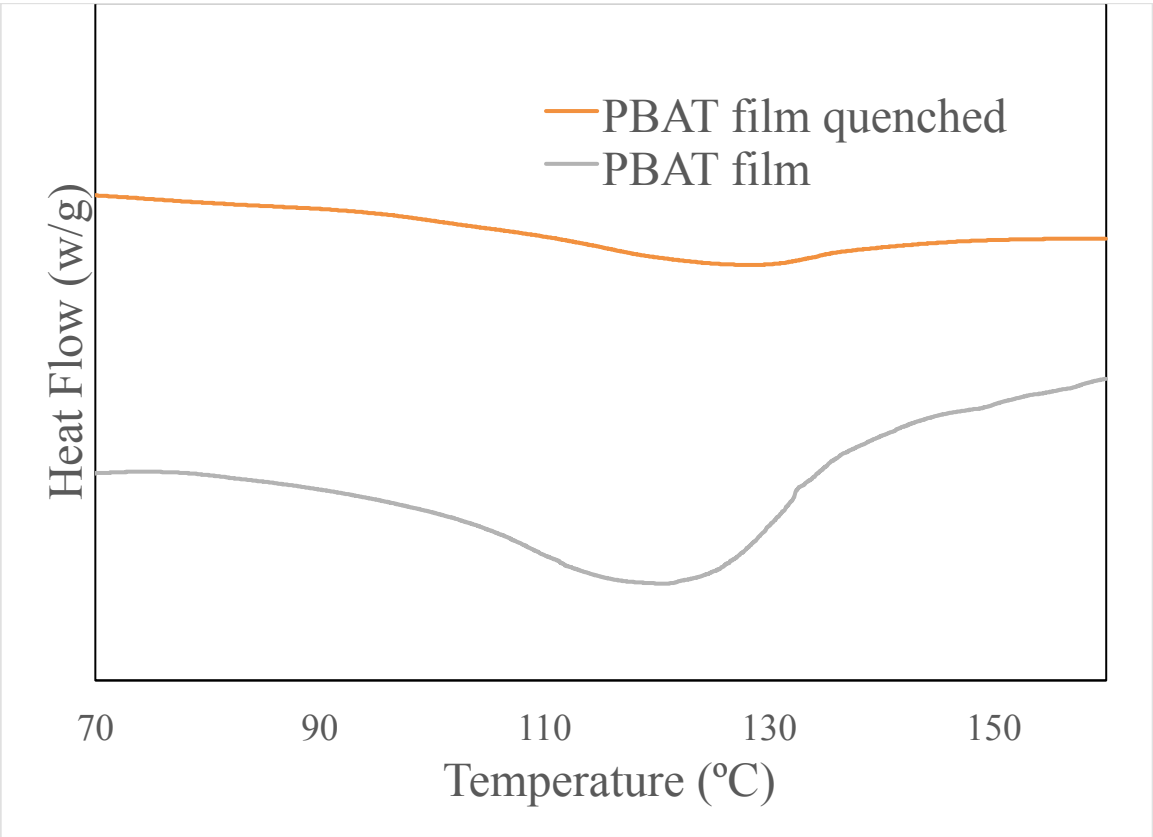

Figure 6.3-1 DSC curve of PBAT after film cast process and its melt quenched sample

6.3.3 Scanning Electron Microscopy (SEM)

Two methods were used to determine the morphology of the blends depending on the content of PBAT. First, blends samples with 20wt% and 40wt% PBAT were glued on the top of molded epoxy resin, then microtomed parallel to its surface using a Leica RM2165 microtome equipped with a liquid nitrogen chamber at -100°C and finally coated with gold. The films were Cryo- microtomed on the surface of MD-TD plane. Preparation of low PBAT content samples using this method was not promising and we used second method, described thereafter, to analyze their morphology. Samples with low PBAT content are less flexible and Cryo-fracture method is more practical. These samples break with fairly sharp surface in liquid nitrogen while blends with higher PBAT show some stretching and higher roughness on break surfaces. Cryo-fractured samples with low PBAT content (5% and 10%) were then coated with gold for SEM analysis. A high resolution Hitachi S-4700 microscope operated at 2 kV accelerating voltage was employed for FEG-SEM

6.3.4 Mechanical Tests

Both tensile and puncture tests were performed on the films using an Instron ElectroPuls 3000 equipment (Norwood, MA),USA. Puncture tests were performed in compression mode using a puncture accessory tool provided with the apparatus and in accordance with ASTM D5748-95(ASTM D5748-95 2012) with a 500 N load cell. Tensile test were performed with accordance to ASTM D882-12 and speed of 5 mm/s.(Lourenço et al., 2012)

6.3.5 Self-adhesion (Hot-tack)

Lab scale SL100 Lako-Tool instrument, Lako Tool & Manufacturing, Inc.USA., was utilized to investigate self-adhesion behavior of the prepared blends film samples. The tests were performed under the specifications mentioned in the ASTM F1921 / F1921M-12e1 experimental methods. (ASTM F1921 / F1921M-12e1 2012) Metallic jaws covered by Teflon were used and the sealed area was 19.1mm×25.4mm on sample strips 25.4mm width×330.2mm length. The pressure was set to 0.5 N/mm^2 and the dwell time fixed for all samples at 1s.

6.4 Results and discussions

6.4.1 Thermal analysis

In order to investigate the effect of thermal treatment on the crystallinity of the PBAT samples, a differential scanning colorimetric investigation was performed on PBAT films right after production and after quenching. Crystallinity of films decreased significantly by quenching the films from molten state reducing the crystal content of films from 14% to 1.2% as shown in Figure 6.3-1. The other method we used to prevent PBAT molecular chains to undergo orientation and stop the formation of crystals is blending. Laredo et al have shown the effectiveness of this method in blends of PLA/ PCL. (Newman et al., 2009)

Other researchers have investigated the crystallinity of blends of PLA and PBAT. In crystalline PLA, cold crystallization temperature is overlapping with melting temperature window of PBAT and creating difficulties measuring PBAT crystallinity in its blends with crystalline PLA. (Al-Itry et al., 2012; Taib et al., 2012; Xiao et al., 2009)

We were able to resolve this problem with using amorphous PLA resin. Amorphous PLA is a copolymer made from D and L monomers which presents no crystallization and melting point throughout the whole temperature window from 70 ºC to 180 ºC. This method gives us the

opportunity to analyze the change in crystallinity of PBAT as a function of blend content. The calculated crystallization results of the blends are presented in Figure 6.4-1. The percent of crystallinity was calculated using the heat of fusion of fully crystalline PBAT ($\Delta H_{f100} = 114 j/g$) (Chivrac et al., 2006)using equation (5.4-1)

$$X_C = \frac{\Delta H_{fbi}}{\Delta H_{f100}} \times \frac{1}{\varphi} \quad eq\ 5.4-1$$

Where φ is the content of PBAT in the blends and ΔH_{fbi} is obtained from the DSC curve of each blend.

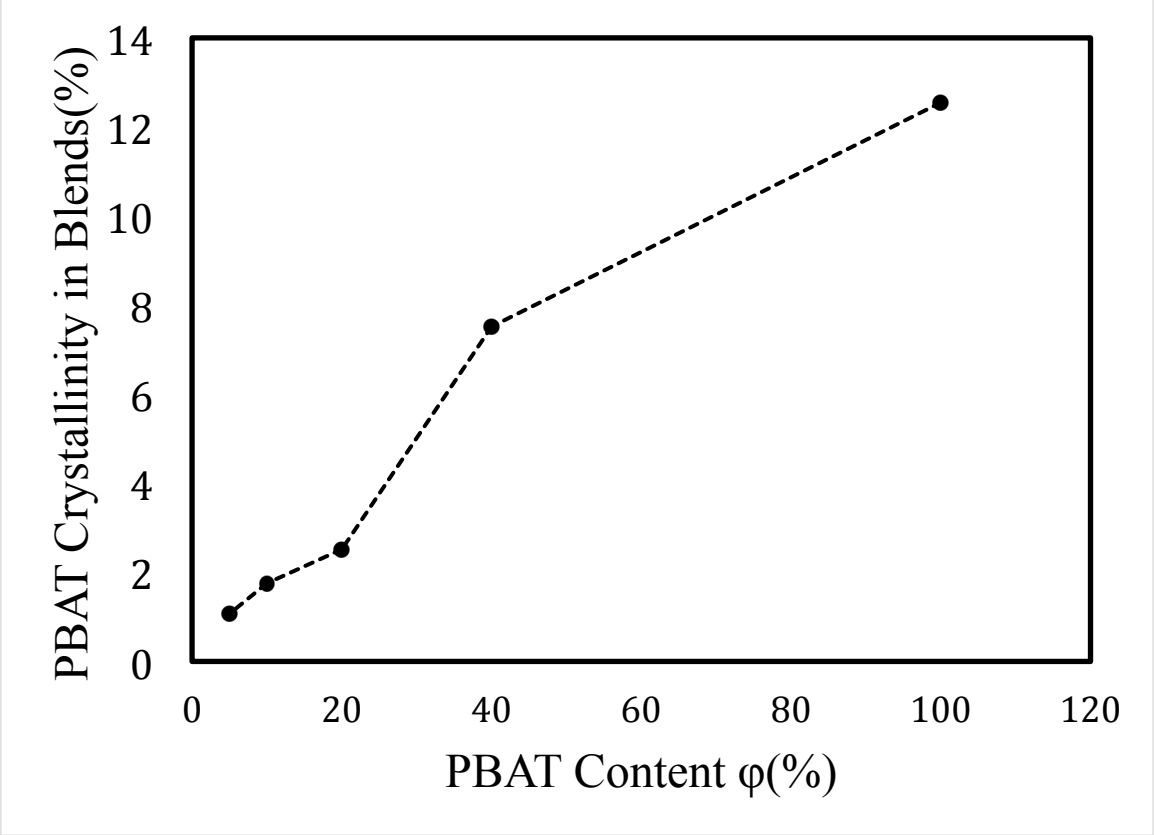

Figure 6.4-1 PBAT crystallinity as a function of PBAT content in blends

Thermal analysis of the blends shows a significant effect of PLA concentration on crystallinity of PBAT. The blends with PLA concentration higher than 60% have a very low crystal content, indicating that the phase separated PBAT domains are having almost amorphous structure compared to pure PBAT film. This lower crystallinity was related to the lower chain mobility of PBAT in the blends due to the hindering effect of PLA.

6.4.2 Self-adhesion

The investigation of self-adhesion of a film requires the determination of the main characteristics.(Meka & Stehling, 1994; Mueller et al., 1998; Najarzadeh & Ajji, 2014b; Stehling & Meka, 1994) First self-adhesion initiation temperature (T_{si}) which indicate the temperature at which two surface would adhere together at a certain pressure and time to reach a required force of debonding (200g/25.5mm for our tests). Increasing temperature from this temperature ($T>T_{si}$) will result in better diffusion and hence better adhesion. (Meka & Stehling, 1994; Mueller et al., 1998; Najarzadeh & Ajji, 2014b; Najarzadeh et al., 2014; Qureshi et al., 2001; Wool & O'connor, 1981; Wool, 1995) Figures 3 and 4 present the self-adhesion strength of PLA resin compared with PBAT and amorphous PBAT and also the self-adhesion of their blends respectively. Two other temperatures are also as important; plateau initiation temperatureT_{ip} and plateau final temperature T_{fp} are the window of temperature between which the force of debonding is at its maximum and remains almost constant. The last parameter is the plateau strength that gives the maximum force of debonding obtained through the self-adhesion process.(Meka & Stehling, 1994; Najarzadeh & Ajji, 2014b; Najarzadeh et al., 2014; Stehling & Meka, 1994) We focus on the change in self-adhesion temperature as a function of crystal content of the blends.

The study of the healing of amorphous PET(Boiko et al., 2001) done by Prud'homme et al. showed that amorphous polymers can have a lower T_g on the surface than in the bulk. The reason for this difference originates from the difference in segment distribution on the surface of amorphous polymeric products than in its bulk, leading to higher number of chain ends on the surface.(Boiko et al., 2001; Boiko & Prud'homme, 1999; Boiko & Prud'homme, 1998; Mayes, 1994) Segregation of chain ends on the surface of a polymer at a close distance (d) to the surface in comparison to the chain radius of gyration R_g (i.e. $d \geq 2R_g$), can be regarded as different polymer with lower molecular weight and hence lower T_g. (de Gennes, 1992; de Gennes, 2000; Mayes, 1994) The lower T_g will result in higher mobility, higher diffusion and thus higher adhesion strength at lower temperatures.(Boiko et al., 2001; Boiko & Prud'homme, 1999; Boiko & Prud'homme, 1998) Figure 6.4-2 shows the effect of removing the crystalline structure of PBAT through thermal treatment. It is clearly observed that it can result in lower (T_{si}).

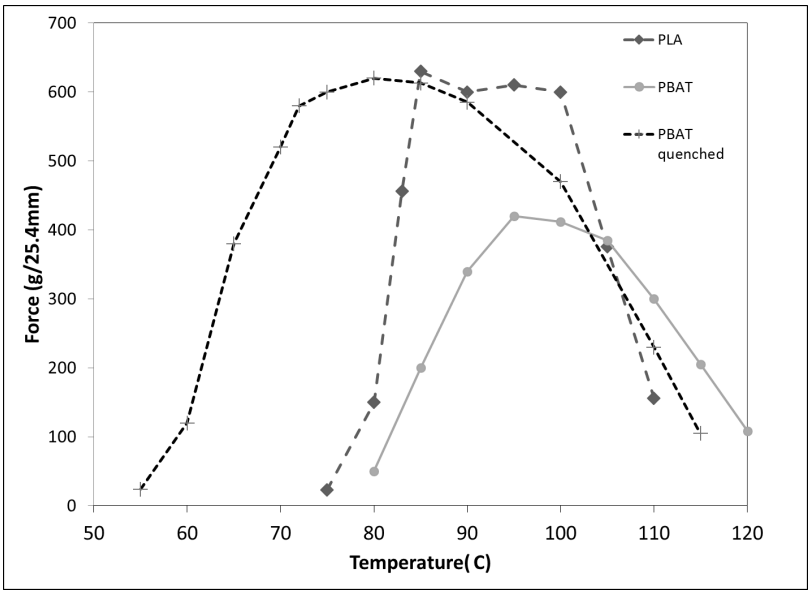

Figure 6.4-2 Effect of crystallinity on the self-adhesion properties of PBAT

Application of a layer of amorphous PBAT results in higher chain mobility on the surface of the film, which leads to higher diffusion and higher number of possible entanglement at the healed surfaces. (Boiko et al., 2001; Prager & Tirrell, 1981; Wool et al., 1989) As our measurement are performed immediately after the seal formation, the melt viscosity of the surface play an important role. Higher viscosity and mechanical strength will increase the force measured for debonding. In other word, considering the softening behavior of polymeric materials by temperature, the higher the hot-tack initiation temperature (T_{si}) the higher the chance for the material to have a lower viscosity and lower mechanical strength, which will result in lower debonding work at relatively high temperatures. (Ajji et al., 1986; Byron Bird & Carreau, 1968; Lacroix et al., 1997; Mueller et al., 1998; Najarzadeh & Ajji, 2014b; Najarzadeh et al., 2014; Qureshi et al., 2001)

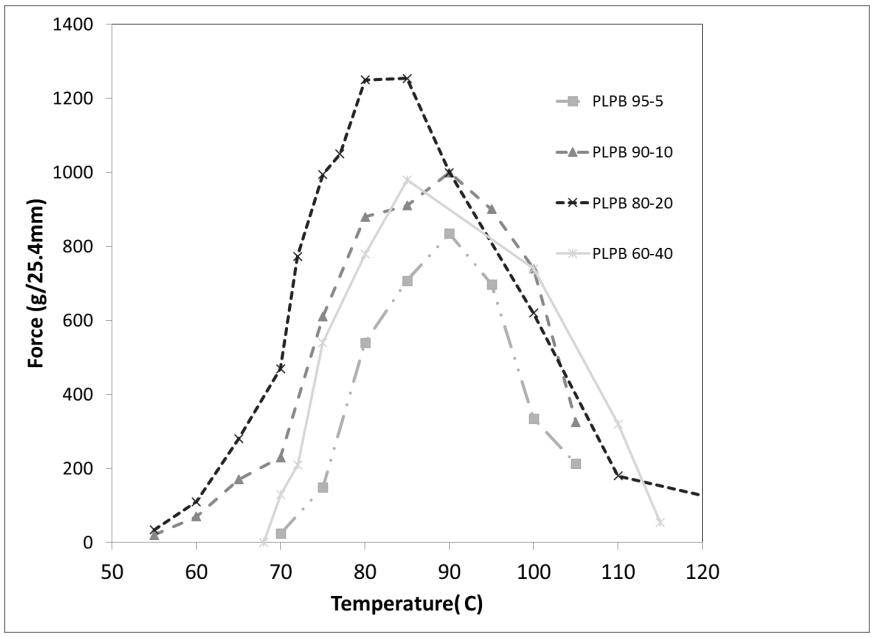

Figure 6.4-3 Hot-tack results of PLA/PBAT blends

Blends of PLA with (PBAT) have been studied by many research teams in the past.(Chiu et al., 2013; Jiang et al., 2005; Weng et al., 2013; Xiao et al., 2009; Zhang et al., 2012) The possibility for PBAT to act as an impact modifier and its capability to affect the biodegradability behavior are some of the advantages of these blends. (Al-Itry et al., 2012; Weng et al., 2013)

The results of self-adhesion of the blends presented in Figure 6.4-3 illustrate the effectiveness of addition of PBAT to PLA in terms of lowering the hot-tack initiation temperature of the blends. This shift of up to 20°C lower than (T_{si}) of pure resins indicate the significant effect of lower crystallinity of PBAT in the blends. The study of the morphology of these blends from SEM micrographs, shown in figure 5, reveal large deformation of the dispersed phase into ellipsoids. This morphology will provide the blend films with high aspect ratio of PBAT dispersed phase(Ajji et al., 1992; Ajji & Utracki, 1996; Harrats et al., 2005; Stegeman et al., 1999). The significant effect of PLA concentration on lowering the crystallinity of PBAT, discussed above, prevent elongated PBAT domain in the blends of 5% to 20% PBAT content to have high crystallinity.

Decreasing the crystallinity of PBAT via blending shifts the behavior of the resin toward that of amorphous PBAT($T_{si_{blends}} < T_{si_{PLA}} \& T_{si_{PBAT}}$). On the other hand, by further increasing PLA content, the effect of the change in crystallinity will be counterbalanced by the rigidity and

lower mobility of abundant PLA molecular chains, leading to higher hot-tack initiation temperature.

Because of the decrease of T_{si} of Blends, the temperature window at which the self-adhesion force is practically acceptable (i.e hot-tack force above 200 g/25.4mm) increases significantly, which will provide a wider operational window for these blends.

6.4.3 Morphology study

To better understand the morphology of blends, prepared samples' surfaces were observed using Scanning electron microscopy. The micrographs are presented in Figure 5. Phase separation and matrix/disperse phase morphology have been reported by many researchers at different concentrations of PLA/PBAT. (Jiang et al., 2005; Lee et al., 2007; Signori et al., 2009; Zhang et al., 2009) None of these works have addressed the effect of elongational flow on the deformation of the dispersed phase.

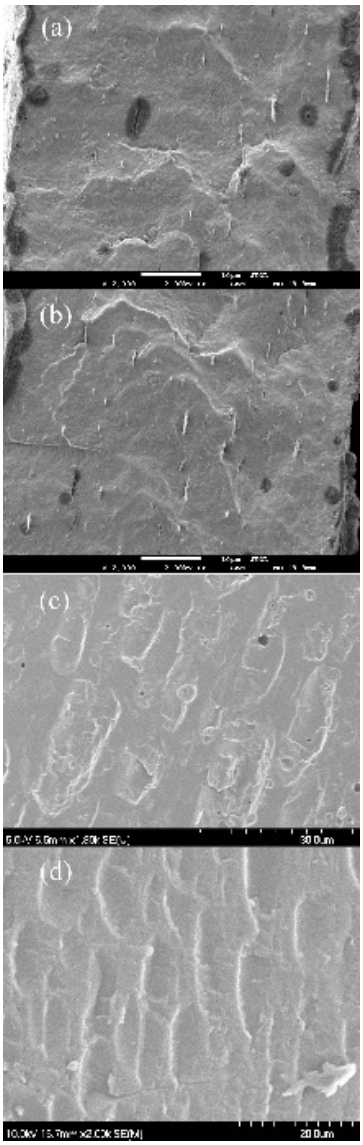

Figure 6.4-4 SEM micrographs of Cryo-fractured blends (a) PLPB95-5 sample (b) PLPB90-10 sample and microtomed surfaces (c) PLPB80-20 and (d) PLPB 60-40.

As was shown previously(Najarzadeh et al., 2014), the blends films show elongated morphology due to the elongational flow field present in the cast film process. By increasing the dispersed phase content, the amount of surface covered by its ellipsoidal droplets will increase, which is clearly observed in Figure 5(c,d), increasing the chances for a better adhesion during hot-tack, which is in agreement with the results presented in Figure 6.4-3. The increase of PBAT over 20% will provide larger dispersed domains, which will have higher

crystallinity preventing the blends to self-adhere at lower temperatures as also illustrated in Figure 6.4-3.

6.4.4 Puncture Resistance

An acceptable seal layer must show also good mechanical properties, which are of great importance in packaging applications. PLA's low flexibility and brittleness cause pin-holing and loss of package barrier properties. The puncture resistance measures the resistance of the films to penetration at standard low rate.(ASTM D5748-95 2012) Puncture resistance can also be improved as a result of blending as shown in Table 6-3. Increasing the content of PBAT in the blends results in higher flexibility and better punctures resistance. The results obtained from Stress- Strain test of the samples were also used to calculate their energy of deformation (Toughness)(Lourenço et al., 2012; Newman & Strella, 1965) form their stress- strain curve. The toughness results are also presented in Table 6-3.

Table 6-3 The mechanical properties of PLA/PBAT blends. Puncture resistance data are collected in compression mode

Sample	Maximum Puncture Load (N)	Puncture strain at Maximum Puncture Load (%)	Puncture Energy at Break (mJ)	Tensile energy of deformation at break (MJ/m^3)	Tensile Strength at Yeild (MPa)
PLA	7.21±0.57	6.52±0.27	10.77±1.29	1.56±0.06	50.62±1.15
PLPB95-5	17.30±1.54	28.18±3.30	104.92±16.57	8.23±0.57	48.11±2.03
PLPB 90-10	21.69±1.03	28.87±1.39	114.74±10.90	11.56±0.74	45.23±2.13
PLPB 20-80	13.7±0.95	32.30±2.94	65.37±10.48	17.06±2.90	38.80±1.54
PLPB 60-40	9.45±0.92	39.23±1.11	49.6±5.89	75.46±22.63	34.44±2.11
PBAT	4.96±.15	65.15±1.49	43.05±2.36	63±2.50	20±0.32

Many researcher have shown that by increasing the content of PBAT in PLA blends, the toughness increase gradually(Anderson et al., 2008; Garlotta, 2001; Jiang et al., 2005; Lee et al., 2007). Comparing the puncture energy at break (E_{PB}) and Toughness of the blends shows that, in blends containing more than 10% of PBAT, the E_{PB} start decreasing although their toughness is still increasing.

This improvement in puncture resistance and toughness for all blend samples compared to PLA provide safe-handling features for packages produced using these blends.

6.5 Conclusion

Self-adhesion initiation temperature of semi-crystalline poly (butylene adipate-*co*-terephthalate) were shown to have great dependency on its crystallinity. Quenching was shown to

be an appropriate method to remove its crystalline structure and encourage the higher chain mobility and lower hot-tack initiation temperature. Restricting chain mobility through blending with poly(lactic acid) has also been able to successfully reduce the crystallinity of PBAT. Self-adhesion initiation temperature of PLA/PBAT blends is a function of crystallinity of PBAT and content of PLA in the blends. Lower crystallinity of PBAT provide the blends with higher mobility while the higher content of PLA's rigid molecular chain reduces the blends ability to diffuse and bond at the interface. As a result of blending, hot-tack initiation temperature decrease up to 20ºC at 20% of PBAT in blends, which is significant for many practical applications. Toughness of the blends increases as the content of PBAT increases. The blends show a significantly higher puncture resistance. The puncture resistance show a maximum at 10% of PBAT in the blends. Both toughness and puncture resistance are important to maintain the integrity of sealed packages.

6.6 Aknowledgement

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CHAPTER 7 ARTICLE 3: SELECTIVE DEGRADATION OF BIODEGRADABLE BLENDS IN SIMULATED LABORATORY COMPOSTING

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7.1 Abstract

ATR-Fourier Transform infrared technique was used in combination with lab scale composting setup to investigate the selective composting of two-phase biodegradable blends based on Polylactic acid (PLA) or Poly(hydroxy butyrate) (PHB), toughened through melt blending with poly(butylene adipate-co-terephthalate) (PBAT), referred to as PLPT50 and PHPT50 respectively. All samples have been processed into films of 35μm thickness by means of cast film process. The simulated lab scale composting setup with gas collection columns was used to measure cumulatively evolved CO_2 gas as an indication of extent of biodegradation. The results from gas collection revealed a decrease in the rate of CO_2 evolution as a consequence of blending. ATR-FTIR spectroscopy detected two distinctive C=O ester bonds for PLPT50, PLA (1743 cm^{-1})/PBAT (1710 cm^{-1}), and also PHPT50, PHB (1720 cm^{-1})/PBAT (1710 cm^{-1}), indicating the phase separated morphology of blends. The absorption ratio of C=O bond for PLA and PHB decreased gradually as a function of composting time leading to a decreased ratio of PLA/PBAT and PHB/PBAT ester bond absorption in the blends. SEM micrographs showed the formation of a porous three dimensional (3D) network for both PLPT50 and PHPT50 through composting after 15 days. ATR-FTIR analysis shows that they are rich in PBAT content, thus indicating selective degradation of the PLA or PHB components in the blends. Investigation of the mechanical properties of the blends demonstrated a gradual loss of Young's modulus caused by the formation of defects through active microbial degradation and hydrolysis.

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7.2 Introduction

A shift toward elimination and reduction of the adverse effects of plastics in landfills and municipal wastes has provided many plastic manufacturers the opportunity to perceive the potential market of degradable polymers.(2012; Bohlmann, 2004; Garlotta, 2001; Grima et al., 2000; Lucas et al., 2008; Shah et al., 2008) Recently, by further developments in technologies involved in production of bio-plastics, many research works have been dedicated to the development of processable blends from bio-based and biodegradable resins, with defined mechanical and morphological properties.(Ganjyal et al., 2007; Garlotta, 2001; Najarzadeh et al., 2014; Pradhan et al., 2010; Pushpadass et al., 2010; Sinclair, 1996; Siracusa et al., 2008) These blends can then be converted into plastic articles with the capability to degrade in composting environments and landfills.(Bocchini et al., 2010; Cha & Chinnan, 2004; Garlotta, 2001; Ghorpade et al., 2001; Narayan, 1991; Yasuda et al., 2011)

Production of high quality high performance articles from bio-plastics is limited, due to their poor performances; particularly their mechanical, barrier and processing related properties. (Sinclair, 1996) In packaging applications and film production industries, Poly(lactic acid) (PLA) has attracted much of the attention due to its good optical properties, high tensile strength and high modulus as well as its capability to be compostable.(Nampoothiri et al., 2010; Sinclair, 1996; Siracusa et al., 2008; Tabatabaei & Ajji, 2012) Available commercial competitors to PLA are Poly(hydroxy alkanoates) (PHAs), which are not optically and mechanically advantageous.(Khardenavis et al., 2007; Marang et al., 2013; Miguel et al., 1997; Reddy et al., 2003; Venkata Mohan & Venkateswar Reddy, 2013) However, their low production carbon footprint and their ability to be manipulated in production line by addition of co-monomers provide them with a potential to overcome many shortages. (Bucci et al., 2005; Miguel et al., 1997)

Both PLA and PHB show brittle behavior and need to be modified before or through processing.(Bucci et al., 2005; Kumar et al., 2010; Sinclair, 1996)Blending has proven to be a promising technique to improve toughness of both resins.(Anderson et al., 2008; Cabedo et al., 2006; Jiang et al., 2005; Lee et al., 2007; Park et al., 2000; Siparsky et al., 1997; Takayama et al., 2006; Vogel et al., 2008a) Modifying resins of interest consist of elastomers or many polyester resins as well as polar modified resins, with low stiffness and high elongation at break.(Bitinis et

al., 2011; Hashima et al., 2010; Pongtanayut et al., 2013) Recently, an approach toward modification and toughening of PLA and PHB using biodegradable aliphatic polyesters or aliphatic and aromatic co-polyesters has shown many advantages as these blends will still remain biodegradable to some extent. (Anderson et al., 2008; Bucci et al., 2005; Liu et al., 2010) (Zhang et al., 2012)

Some studies showed the effect of blending on the rate of disintegration of bio-plastic films in soil, simulated landfill and marine water as well as aquatic environments and industrial compost facilities. (Arias et al., 2013; Briassoulis et al., 2010; Grizzi et al., 1995; Kale et al., 2007; Lucas et al., 2008; Nampoothiri et al., 2010; Tosin et al., 1996) These rates vary depending on the chemical structure of the resin, activity of soil and composts and the depth at which the samples are buried. To the best of our knowledge, no correlation between the behaviors of each phase in the blends and the rate and mechanism of biodegradation of blend's components have been studied. Published works on the degradation behavior of blends, have tried to relate the cumulative behavior of biodegradable films and articles, e.g. total CO_2 evolution and total weight loss, to their degradation and composting rate. (Arias et al., 2013; Briassoulis et al., 2010; Ganjyal et al., 2007; Grizzi et al., 1995; Kale et al., 2007; Lucas et al., 2008; Nampoothiri et al., 2010; Tosin et al., 1996)

As mentioned above, measurement of evolved CO2 is one of the techniques that can quantitatively determine the rate of degradation of the whole product, under aerobic active microbial conditions, as addressed by the ASTMD6400(ASTM D6400 2012; Cossu et al., 2011; Kale et al., 2007). Other techniques to determine the rate of degradation of a product include weight loss measurement, monitoring molecular weight change and the change in mechanical properties of the test products.(Briassoulis et al., 2010; Nampoothiri et al., 2010; Tosin et al., 1996) Nevertheless, none of these techniques can provide with a detailed structural change through blends degradation. (Briassoulis et al., 2010; Nampoothiri et al., 2010)

Due to close polarity of ester bonding and low interfacial tension between aliphatic polyesters, extraction and detection of phases using solvents is practically impossible. Vogel et al. showed the capability of FTIR spectroscopy in the analysis of phase separation and phase morphology of two-phase blends of biodegradable polyesters. (Vogel et al., 2008a; Vogel et al., 2008b) In a recent study by Braun et al., determination of monomer content in Poly (lactic acid) has been addressed by an FTIR assisted method.(Braun et al., 2006) They indicated the

development of a double peak that corresponds to monomer absorption band in the spectrum range of 1400cm^{-1}to 1500cm^{-1}. FTIR technique have been also used to follow the change in the chemical structure of polymers after degradation. Few works address the successful use of FTIR in following degradation of pure biodegradable plastics after composting.(Agarwal et al., 1998; Cossu et al., 2011) Capability of FTIR spectroscopy to differentiate PLA form its monomer and also ester bonds of different aliphatic and aromatic polyesters prompted us to combine it with composting in order to determine the selectiveness of microbial and hydrolytic degradation of biodegradable blends. This understanding of phase-wise degradation will assist in future determination of biodegradation rate of blends and multilayer structures made from compostable resins.

7.3 Materials and Methods

Amorphous grade polylactic acid (PLA) obtained from Natureworks, USA, is a copolymer of D&L lactic acid with about 10% D-monomer content. The Poly(hydroxy butyrate) (PHB) commercial grade P209 was obtained from Biomer, Germany. Ecoflex F Blend C1200 was purchased from BASF Plastic Technologies USA. Film samples of pure materials as well as their 50%-50% blends were used for the composting study. This concentration was chosen in order to help in comparing the result with available literature. All the samples have been processed using a twin-screw extruder (Leistritz model ZSE 18 HP co-rotating) into films using a cast film die. The draw down ratio used allowed reducing the films thickness to 35μm.

Spotlight 400, PerkinElmer FTIR spectrometer equipped with ATR accessory was used in the IR range of 600 to 4000 to investigate the film samples. For each spectrum, the data were collected with resolution of 4cm^{-1}. A straight baseline was used from 1400 cm^{-1} to 1500 cm^{-1} for the deconvolution of asymmetric bending mode peak of CH_3. Another straight baseline from 1600 cm^{-1} to 1750 cm^{-1} was used to deconvolute the ester C=O peak.

A laboratory scale setup for composting was built based on ASTM D5338. This system was designed to yield the percentage of carbon dioxide released from the organic carbon content of the samples. Mature compost was obtained from Fafard Company, Canada. To remove non-reacting particles, the compost was filtered using Mesh 4 sieve. The water holding capacity of the compost was determined to be 219% and that of as received compost was 67%. The water content of the compost was adjusted to 70% of its holding capacity. All the film samples were cut

into 5×5 cm^2 pieces and mixed into the 1:6 ratio of the compost. Cellulose filter obtained from Sigma-Aldrich (Milwaukee, WI) was used as positive control. The reported organic content of cellulose is 42.5%. Haake E52 immersion heat controller was used to keep the oil bath temperature constant at 73.5°C. Using this oil bath the resulting composting vessel temperature was determined to be 55 ±3°C. The tests were performed in three replicates and the results averaged. The evolved CO_2 was collected in a gradual cylinder filled with saturated $Ba(OH)_2$ solution(i.e. 0.1 M) and the unreacted solution was neutralized by 0.01M HCL solution. The normalized CO_2 evolution was calculated according to ASTM D 5338. (ASTM D5338 2011)

Parallel to composting, for disintegration test observations and mechanical investigations, strips of 5×2.5 cm^2 of pure samples and their blends were incubated at the same condition as composted samples.

Tensile tests were carried out in accordance to the ASTM D882 on an Instron (Norwood, MA) 3365 universal testing machine equipped with a 500 N load cell and using a crosshead speed of 5 mm/min.

The SEM micrographs where taken using a Jeol JSM 840 scanning electron microscope at 10 to 15 kV and samples have been coated with gold beforehand.

7.4 Results and Discussions

7.4.1 Disintegration tests

Disintegration observation with time of pure and blend samples are depicted in Figure 7.4-1. The results show that the PHB samples disintegrate in the early stages of the test at about 10 days, which is considerably faster than pure PLA as well as their blend with PBAT, which would last unbroken till about 30-45 days of incubation.

The results of PLA disintegration show longer stability compared to published works on thicker samples.(Grizzi et al., 1995; Kale et al., 2007; Siparsky et al., 1998; Wang et al., 2008) The latter would follow the suggested two-step degradation of PLA, which has been proposed by Grizzi et al and Kale et al.(Grizzi et al., 1995; Kale et al., 2007) The hydrolysis, as Grizzi introduces as the first step, is an autocatalytic step and dependent on the thickness of the samples. Grizzi showed the thicker samples in which produced low molecular weight acids need extended time to diffuse outside, would hydrolyze faster than film samples.(Agarwal et al., 1998; Grizzi et

al., 1995; Nampoothiri et al., 2010; Wang et al., 2008) Hydrolysis beside the bacterial degradation is affecting the rate of mechanical weakening shown in Figure 7.4-2. Formation of cracks in composted samples and also development of a 3D porous networks in blends presented in Figure 7.4-3, Figure 7.4-4 and Figure 7.4-5 will affect the disintegration and mechanical properties drastically as will be discussed later. For pure PLA samples and its blends unlike PHB based samples; bacteria cannot directly degrade the polymeric chains and the hydrolysis step play the main role to control the rate of disintegration.(Agarwal et al., 1998) The evidence of hydrolysis of PLA and production of Oligomeric Lactic Acids (OLAs), as a result of composting, is strongly supported by the development of a double peak related to the CH_3 asymmetric bending mode at 1454 illustrated in Figure 7.4-6 and also the development of a double peak in the FTIR spectrum at 1745 cm^{-1}, as shown in Figure 7.4-7, which is related to C=O stretching vibrations.(Braun et al., 2006; Kister et al., 1998)

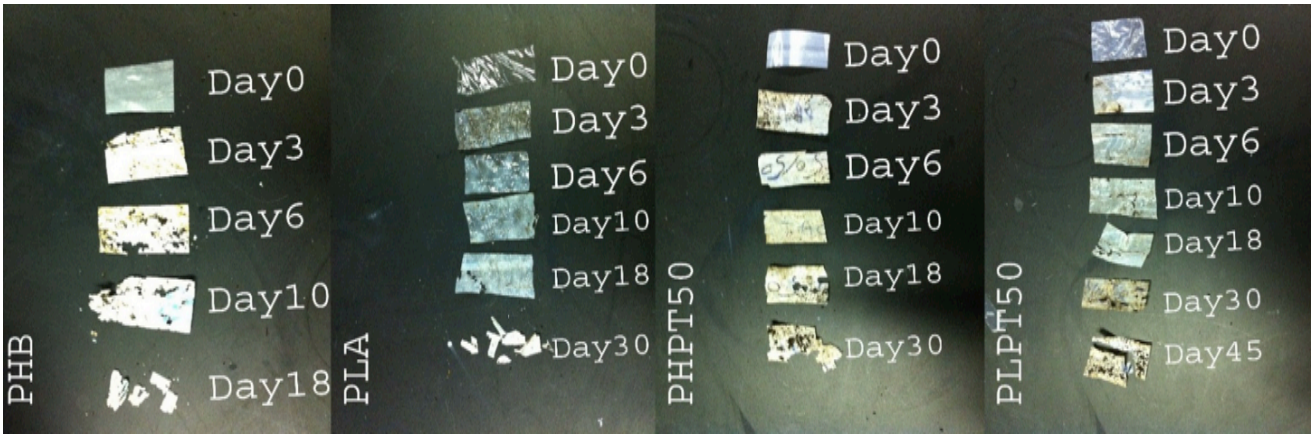


Figure 7.4-1Images of samples at different composting time, pure PLA and PHB are shown together with their 50/50 blends of PLA/PBAT(PLPT50) and 50/50 blend of PHB/PBAT/ (PHPB50).

7.4.2 Mechanical Behavior of Composted Samples

The effect of biodegradation time on the mechanical behavior of samples is illustrated in Figure 7.4-2. Mechanical behavior of the resins and their blends dramatically change as the biodegradation proceeds in the compost. Biodegradation reduces the young's modulus (E) of the samples due to growing defects caused by either hydrolysis or corrosive enzymatic degradation and causing a decrease in molecular weight. (Ochi, 2008; Shogren et al., 2003) As depicted in Figure 7.4-2 PHB shows significantly higher loss in modulus of elasticity compared to pure PLA and PHPT50 and PLPT50 blends. PBAT samples remain almost stable in the first 10 days of composting time. Modulus of PLA samples decrease at early stages of composting but SEM micrographs show no corrosive degradation and cracking at time window lower than 10 days, as illustrated in Figure 7.4-3. This decrease in tensile modulus is attributed to the plasticizing effect of lower molecular weight entities developed through hydrolysis.

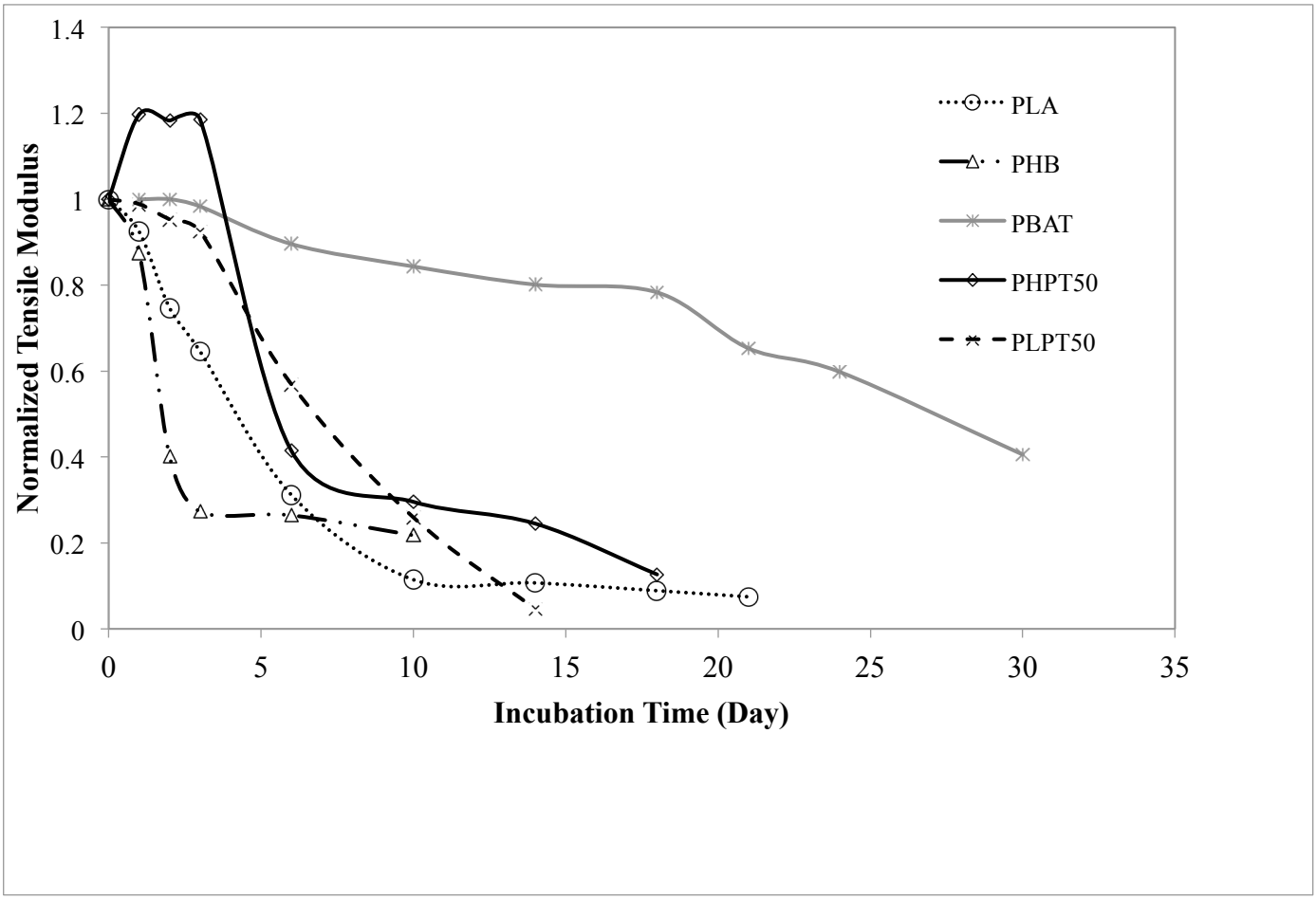


Figure 7.4-2 illustration of the change in the modulus of pure PLA, PHB and PBAT and their blends samples.

As indicated by Hartmann et al.(Hartmann, 1998) the trace of monomer in polymer may have a plasticizing effect, which was also confirmed by the work of Averous et al. (Hartmann, 1998; Martin & Avérous, 2001) Compared to PLA, PHB show sharper decrease in Modulus of elasticity, which is obvious from Figure 7.4-2. The capability of active microbial environment to provide with large number of bacterial species, which can degrade PHB through enzymatic reactions and also the fact, that in contrast to PLA there is no need for hydrolysis to happen before the bacteria can digest the PHB, are mentioned by many researcher to explain the faster degradation of PHB in active microbial environments. (Gilmore et al., 1992; Grima et al., 2000; Manna et al., 1999; Mergaert et al., 1994)

7.4.3 Scanning Electron Microscopy Analysis

SEM micrographs taken at different incubation time and illustrated in Figure 7.4-3 and Figure 7.4-4 reveal, the PHB samples (Figure 7.4-3c and Figure 7.4-3d) have undergone more corrosive biodegradation than PLA pure samples and also PLPT50 and PHPT50 blend samples. PHB is known for its high resistance to hydrolytic degradation.(Bucci et al., 2005; Miguel et al., 1997) The higher rate of biodegradation for PHB is related to a larger number of microbial active species which are able to digest PHB resin as explained above.(Manna & Paul, 2000)

On the other hand, formation of crack and surface roughness, corrosive degradation, in PLA samples is not noticeable till 10 days of composting. As the hydrolysis is the first step in biodegradation of PLA the formation of crack would suggest higher content of hydrolyzed PLA chains. (Grizzi et al., 1995; Wang et al., 2008)

The disintegration of blend samples seems quite different from that of the pure materials and needs a closer and deeper analyzing. As observed in Figure 7.4-1 the blends disintegrate slower. The result obtained are in agreement with the work of Weng et al.(Weng et al., 2013) They have shown that the PLA/PBAT blends are less prone to degradation in soil condition compared to PLA pure samples. But they have found no evidence of change in chemical structure of blends and pure samples in soil.

The SEM images show that the blend samples degrade by microbial activities and leave a 3D porous network, as shown in Figure 7.4-5. The comparative ATR-FTIR spectrums of these

blend samples at different composting times are depicted in Figure 7.4-7 and Figure 7.4-8. The peaks are deconvoluted to enable the quantitative analysis of change in the composition of blends. Results presented in Table 7-1 indicate that these networks are becoming richer in PBAT. Grizzi et al(Grizzi et al., 1995) suggested that, in PLA samples, the autocatalytic degradation of PLA results in the formation of hollow structure in the sample. This phenomenon will help the formation of porous 3D network of PBAT phase, through composting. A thin crust of PLA on both surfaces of PLA samples remains untouched till the diffusion-controlled hydrolysis continues, which is clearly illustrated in Figure 7.4-5.

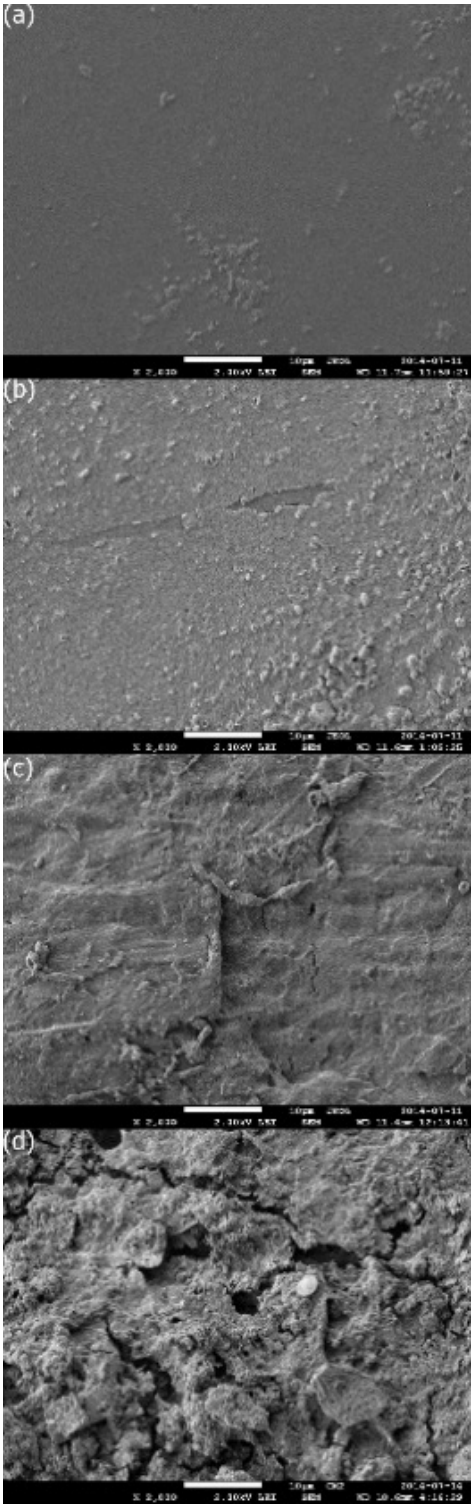


Figure 7.4-3 SEM micrographs after 3rd day (a,c) and 10th day (b,d) of composting for pure PLA(a,c) and pure PHB(c,d) samples.

With regards to the peer-reviewed literatures(Grizzi et al., 1995; Nampoothiri et al., 2010; Wang et al., 2008), degradation of PLA is accelerated by the formation of Oligomeric Lactic Acids and this is due to the fact that in the bulk of the samples, the undiffused lactic acid lowers the pH and acts as a catalyst for the hydrolysis reaction.(Grizzi et al., 1995; Wang et al., 2008)

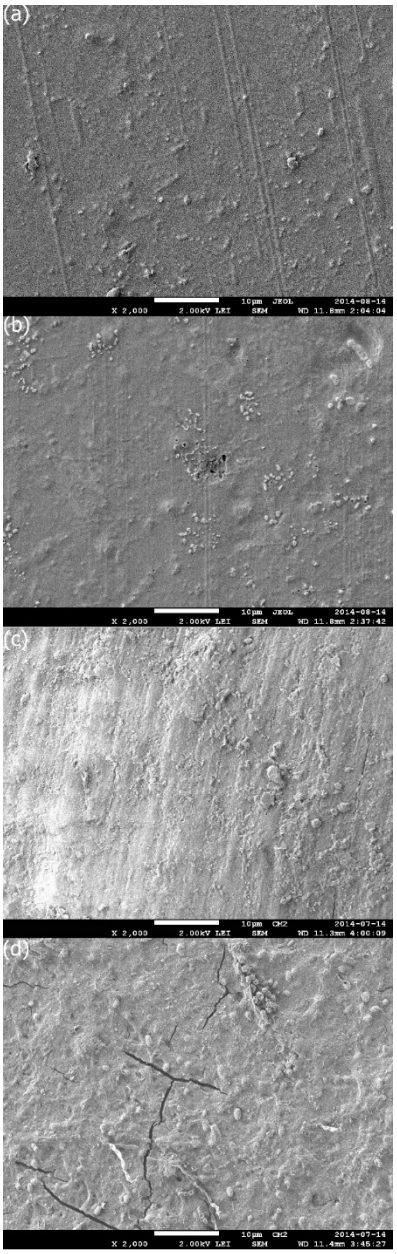


Figure 7.4-4 SEM micrographs of PLPT50 (a,b) and PHPT50 (c,d) at 3 days (a,c) and 10 days (b,d) of composting process

The observation of double peak of CH_3 asymmetric bending mode between 1400 cm^{-1} and 1500 cm^{-1}, shown in Figure 7.4-6, can be related to the formation of lactic acid and OLAs

through said autocatalytic hydrolysis.(Braun et al., 2006; Martin & Avérous, 2001) Bulk hydrolysis mechanism has been suggested for PLA degradation in biotic and abiotic environments by Koeling et al. (Agarwal et al., 1998) They showed that the microbial activity has a negligible effect on the hydrolysis step of degradation, which is the disintegration of ester bonding in PLA resin.

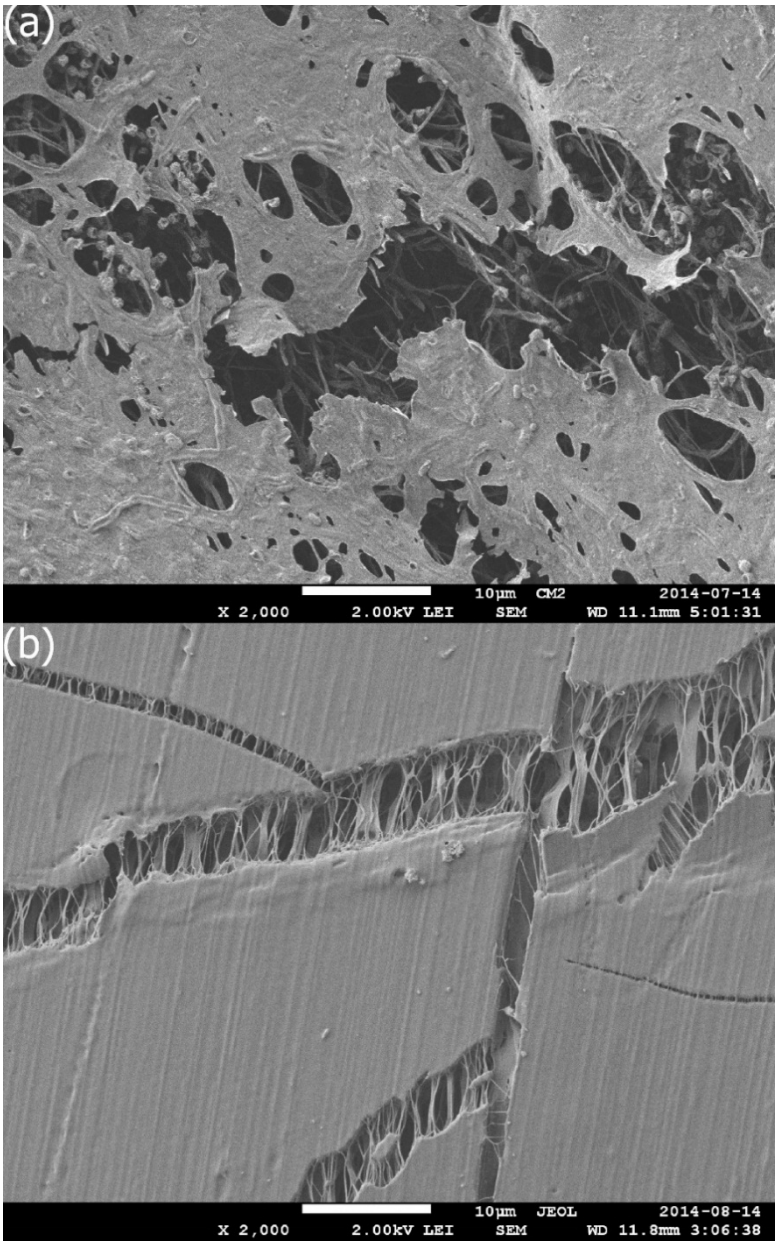
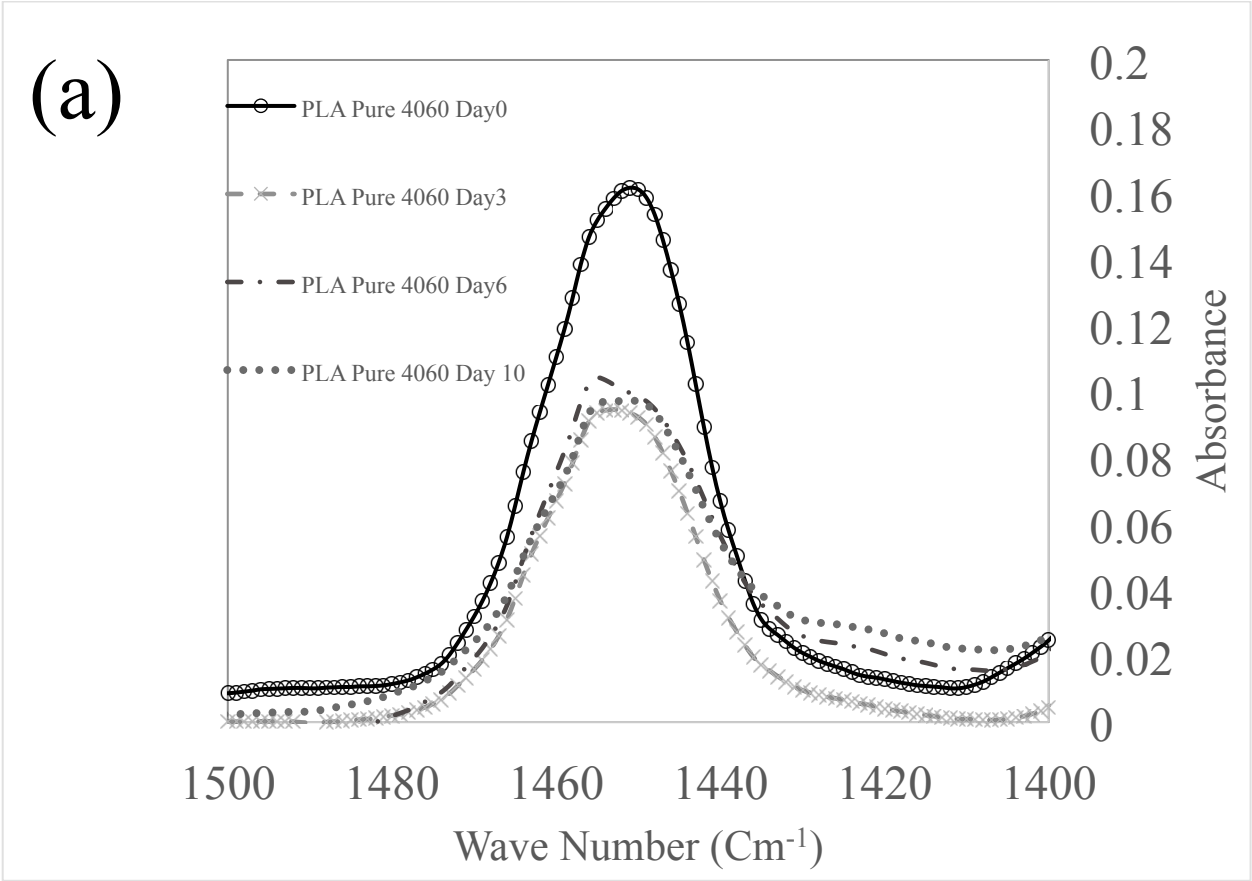


Figure 7.4-5 SEM images of PHPT50 (a) and PLPT50 (b) samples after 15 days of composting.

The ATR-FTIR analysis can also demonstrate that by increasing composting time, the compositions of blends change and the 3D networks formed become reach in PBAT phase. The whole process of composting can then be investigated using this technique as will be discussed below.

7.4.4 ATR-FTIR assisted analysis of the biodegradation process

To better understand the chemical structure and type of bonding, all the samples have been analyzed using ATR-FTIR technique at different times of composting, as presented in Figure 7.4-6a. These Spectra, together with the deconvoluted ones in the range of 1400 cm^{-1} to 1500 cm^{-1} shown in Figure 7.4-6b, illustrate the change in the absorption band of asymmetric bending mode of CH_3 in PLA samples as a function of composting time.



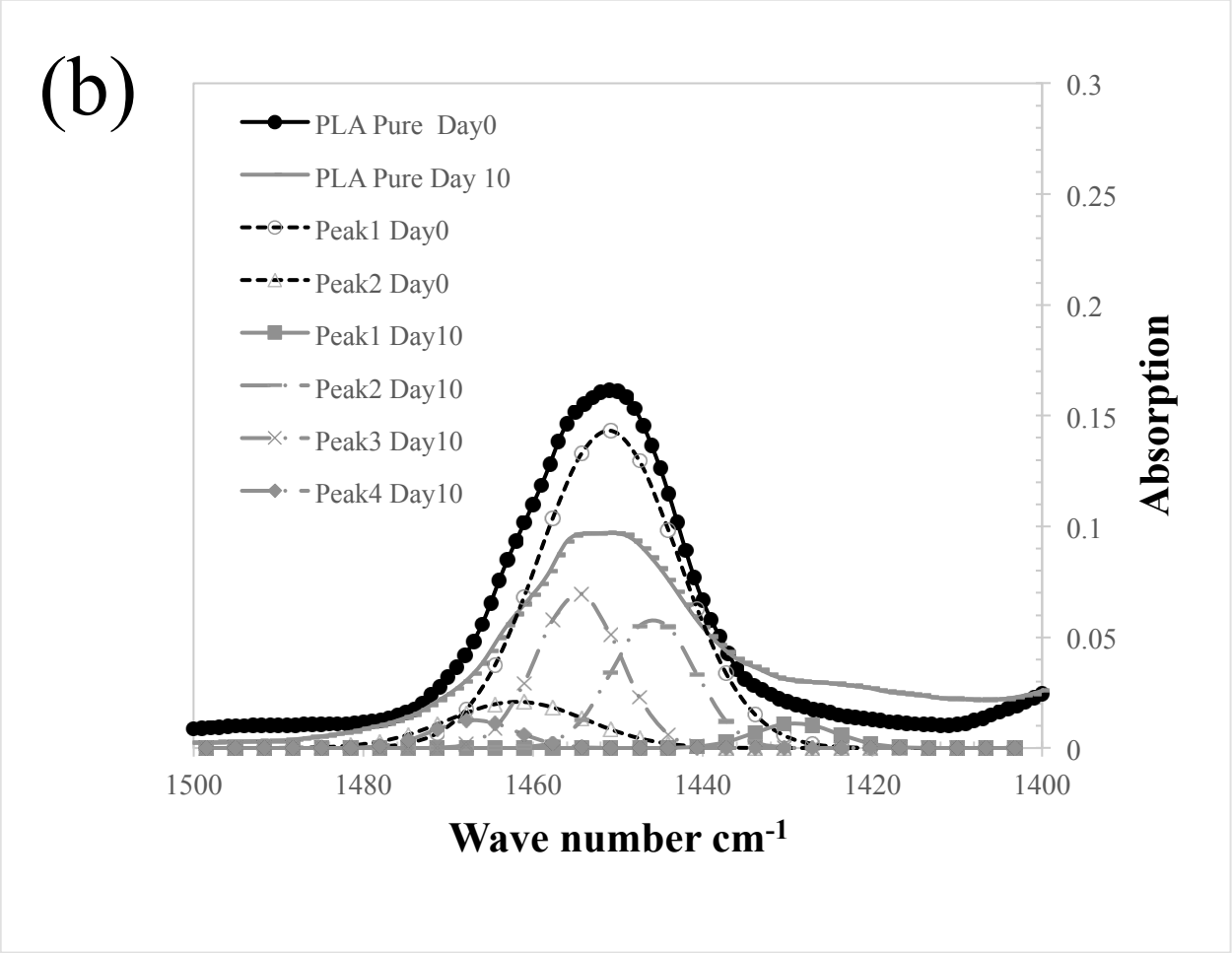


Figure 7.4-6 ATR-FTIR spectrum of pure PLA samples in the range of 1400 cm-1-1500 cm-1: (a) PLA samples at different composting times (0,3,6 and 10 days) and (b) deconvoluted peaks for pure PLA samples at day 0 and the sample tested at day6 of composting.

The development of a double peak at 1454 and 1447 is correlated to PLA and its monomer asymmetric bending mode of CH_3 group. (Braun et al., 2006; Kister et al., 1998) An FTIR assisted technique was introduced by Dorgan et al. to determine the amount of lactide in PLA. The detailed calculations can be found in their study.(Braun et al., 2006)

The results obtained here show that this double peak is developed at early stages of composting, i.e. day 3, and the ratio of monomer to PLA is increasing up to 6 days of composting as illustrated in Figure 7.4-6a and Figure 7.4-6b. Following that, as the composting proceeds, peak ratio decreases indicating lower concentration of monomer in those samples. SEM micrographs represented in Figure 7.4-3 show initiations of cracks on the surface of PLA films at

around day 10, which is in agreement with the decrease of the peak ratio of monomer/PLA given in Table 7-1. Latter can be caused by the release of monomers from the cracked areas.

As depicted by SEM micrographs in Figure 7.4-5, as a result of composting, the samples undergo a selective biodegradation process. 3D Networks that are formed both in PLA and PHB blends have been analyzed using ATR-FTIR spectroscopy. The results are presented in Figure 7.4-7 and Figure 7.4-8. They reveal that, at high composting time, the blends are showing a gradual decrease in the peak ratio of the PHB (1723 cm^{-1}) /PBAT (1711cm^{-1}) and also PLA (1745cm^{-1})/PBAT (1711cm^{-1}) related to C=O stretching absorption band.

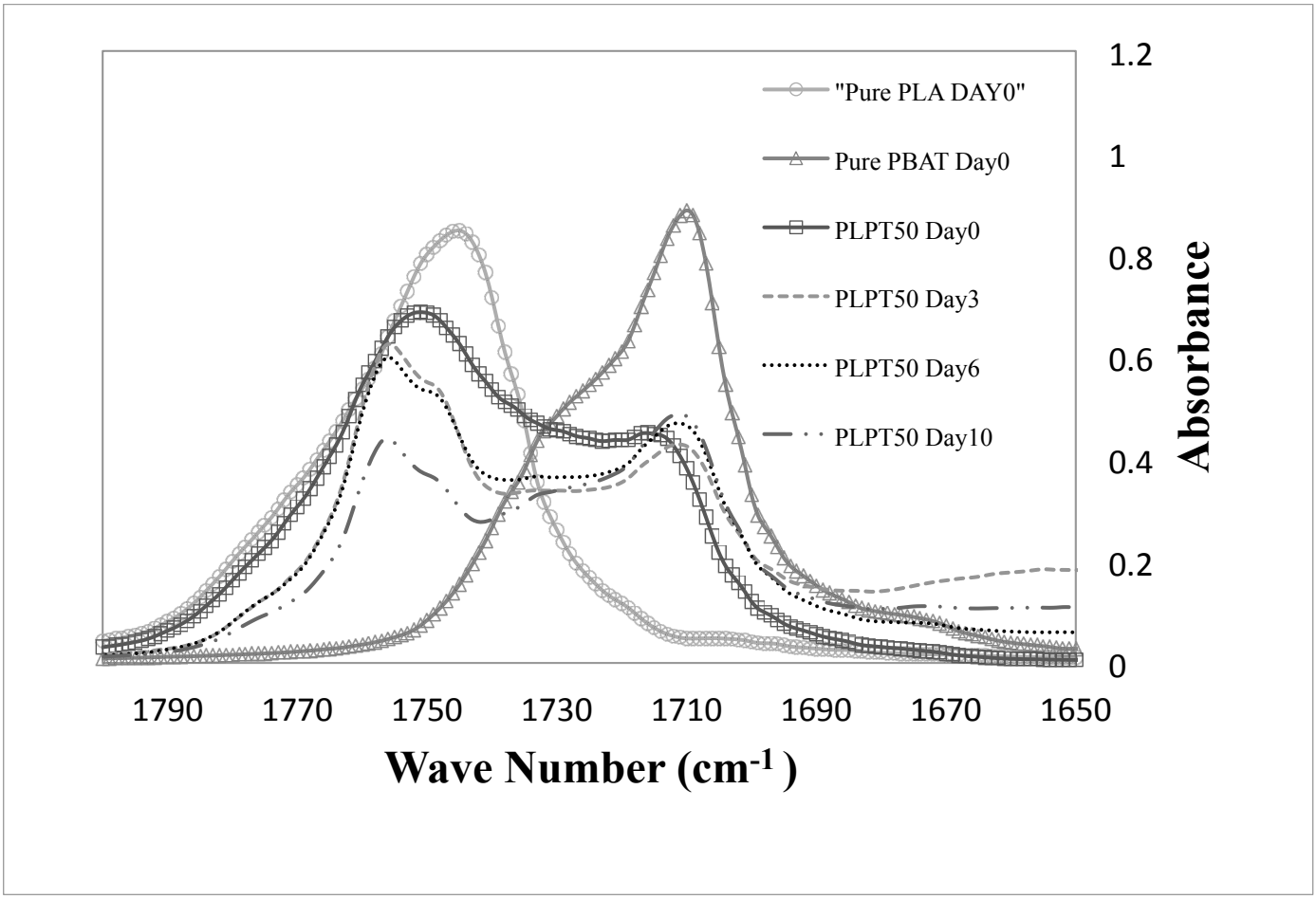


Figure 7.4-7 Change in ATR-FTIR absorption of PLA phase in PLPT50 blend compared to the PBAT phase for various composting times.

To determine the relative quantity of each phase in the blends, FTIR absorption peaks ratio, mentioned above, is to be calculated. Their absorption peak areas have been determined using

peak fit software and a linear base line was used between 1500cm^{-1}and 1800cm^{-1}. The results are presented in Table 7-1 and they strongly suggest the selective composting in blend samples.

Beside that from the results of absorption ratio of CH_3 asymmetric bending presented in Table 7-1 the amount of OLAs in the composted PLA samples show a maximum at around day 6. Latter is in agreement with SEM images which, suggest the release of OLAs by initiation of cracks in the surface of samples at around day 10 of composting shown in Figure 7.4-3 and the results from CO_2 evolution, presented in Figure 7.4-9, that show the threshold of biodegradation for PLA sample at around day 10.

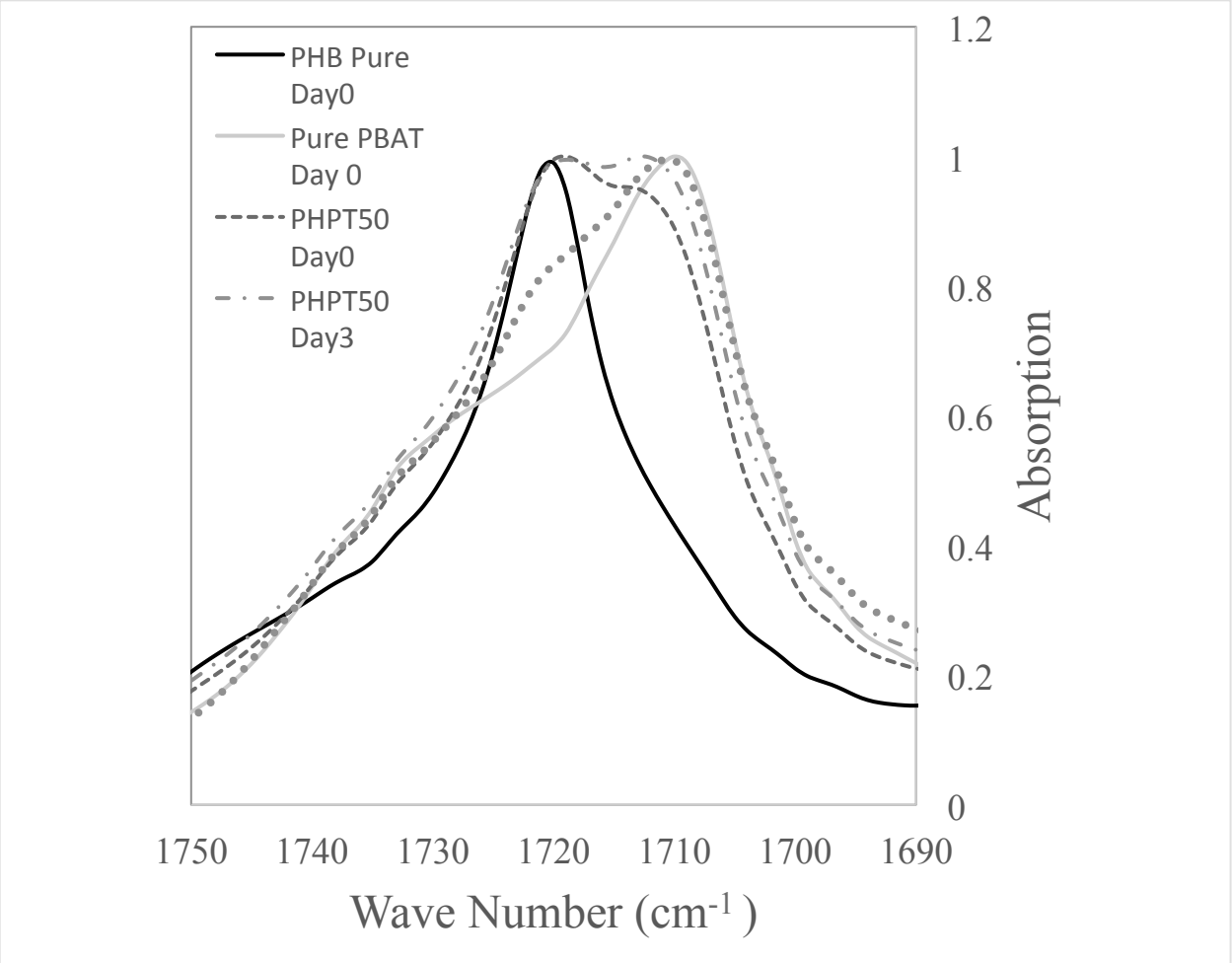


Figure 7.4-8 Evolution of the ratio of absorption of PHB phase in PHPT50 blend compared to the PBAT phase for various composting times.

Table 7-1 : Calculated peak area ratio from deconvoluted FTIR spectrums for pure PLA in range of 1400-1500 cm-1 and for PLPT50 and PHPT50 samples in the range of 1650-1800 cm^{-1}.

Ratio of Peak area	Day0	Day3	Day6	Day10
PLA (1447cm^{-1} /1454cm^{-1})		1.19	1.24	1.2
PLPT50(1750 cm^{-1} /1711 cm^{-1})	1.46	1.30	1.28	1.18
Normalized to day0	1	0.89	0.87	0.80
PHPT50(1723 cm^{-1} /1711 cm^{-1})	1.10	0.97	-	0.71
Normalized to day0	1	0.88	-	0.64

7.4.5 CO_2 Evolution and Composting Results

Measurement of CO_2 evolution during composting of pure and blend samples is the main indicator usually used to determine the rate of composting of biodegradable samples (ASTM D6400 2012; ASTM D5338 2011; Briassoulis et al., 2010; Kale et al., 2007). Figure 7.4-9 shows CO_2 evolution as a function of composting time for four weeks. This graph shows the cumulative CO_2 evolution as a result of bacterial activity. PHB samples have a higher rate of CO_2 evolved, which is expected from higher corrosive degradation observed in SEM micrographs illustrated in Figure 7.4-3. This higher biodegradation rate results in a significant deterioration of mechanical properties as well as faster disintegration of PHB samples, as represented in Figure 7.4-2 and Figure 7.4-1 respectively.

The two-step degradation of PLA samples explained above would let hydrolysis happen before CO_2 evolution starts. The phenomenon is observed to lower PLA samples' modulus of elasticity within the time lag between initiation of composting and CO2 evolution, shown in Figure 7.4-9. These samples become less transparent as hydrolysis continues, which leads to lower ATR-FTIR absorption intensity.(Braun et al., 2006)

CO_2 evolution from composted PLPT50 and PHPT50 samples has similar trends to those of PLA and PHB respectively and the lower normalized CO_2 evolved can be attributed to the lower concentration of PLA and PHB in blend samples compare to pure PLA and PHB. This behavior indicates the selective degradation of blended samples and formation of PBAT rich 3D

porous network. This networks as shown in ATR-FTIR spectrum of Figure 7.4-7 and Figure 7.4-8 indicates that the PLA and PHB phases in the blends with PBAT have higher tendency to degrade in the chosen composting condition.

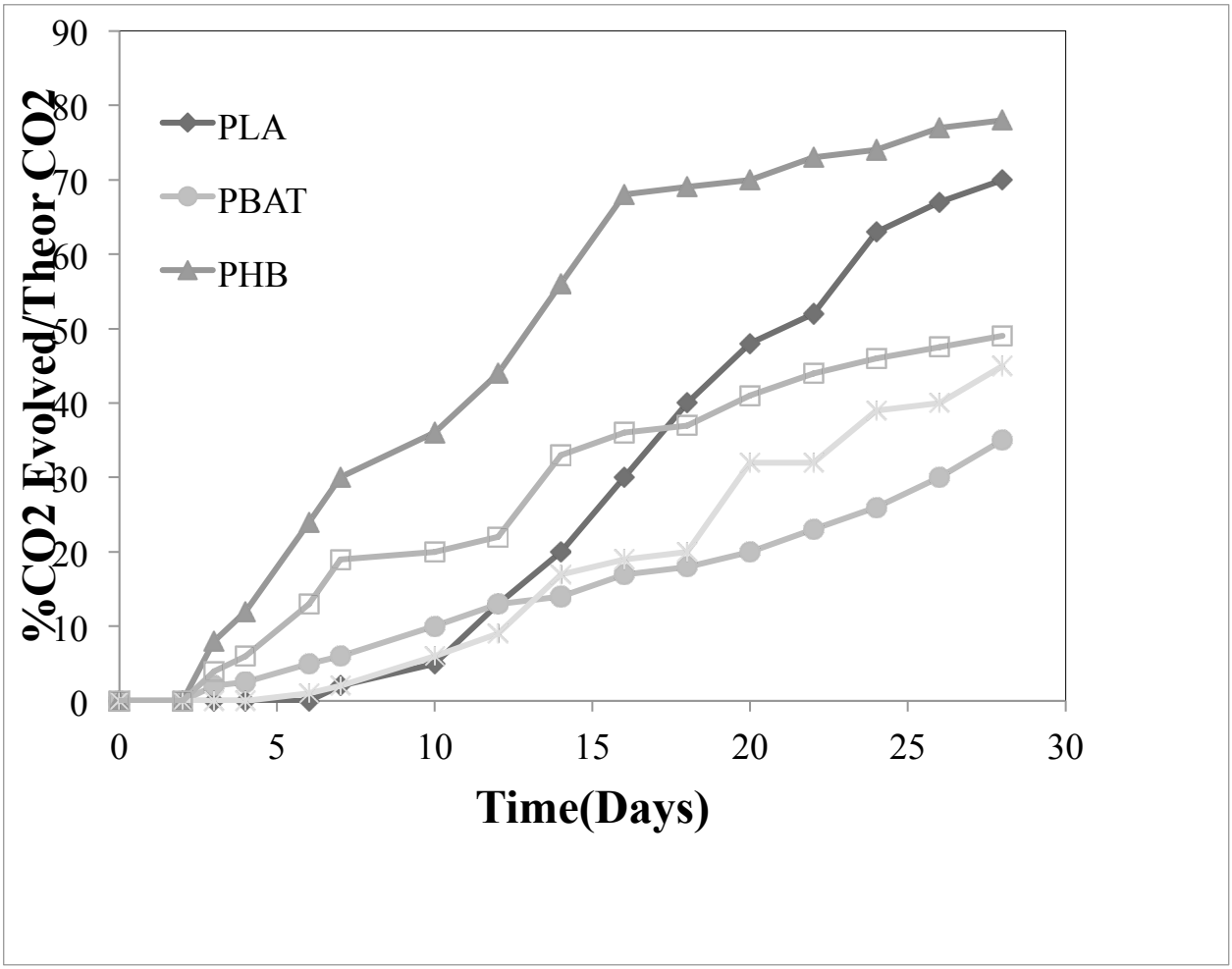


Figure 7.4-9 The rate of CO2 evolution as a function of composting time for pure PLA and PHB and their PLPT50 and PHPT50 blend samples.

7.5 Conclusion

ATR-FTIR spectroscopy is a powerful technique that allows following the changes in the structure of pure and blend samples through the composting process. The peak area ratio of ATR-FTIR spectrum in the range of 1650 cm^{-1} -1800 cm^{-1} in 50-50 wt% blends of PLA with PBAT

and also in 50-50 wt% blends of PHB with PBAT samples have been used as an indication of changes in the composition of these blends through composting time. ATR-FTIR investigation revealed the selectivity of composting to degrade one phase of a blend, i.e. PLA in PLA/PBAT blends and PHB in PHB/PBAT blends, to higher extent and form a porous 3D network. These 3D networks, observed in SEM images, were shown to become rich in PBAT phase as the composting proceeds. Formation of these networks explains the retarded disintegration of the blends. The changes in the mechanical properties show the significant effect of hydrolysis on the softening of PLA samples. Hydrolysis of PLA samples through composting has also been analyzed by the FTIR technique and has been correlated to threshold of CO_2 evolution through composting. As the SEM images reveal cracks would initiate on the surface of PLA samples at around 10days allowing for the higher rate of OLAs diffusion to the compost and more bacterial activity.

7.6 Acknowledgment

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CHAPTER 8 GENERAL DISCUSSION

Replacement of conventional petroleum-based packages, reduction of the amount of this type of plastic and inclusion of biodegradable plastics seem to be inevitable in the future of the packaging industry. The choice of suitable materials, either pure or blends, can be made possible based on a clear understanding of the performances of these resins. This knowledge is a requisite in terms of various properties, among which are their sealability and sealing conditions. Available references mostly focus on the improvement of properties of biodegradable materials in medical applications. Hence these improvements are usually made in order to modify impact strength of devices made of these materials in in-vivo and in-vitro utilization. PLAs and PHAs as main categories of aliphatic polyesters have been debated for packaging applications due to their brittle behavior.

Development of blends with improved tensile toughness and comparatively higher seal and hot-tack strength can be a significant advancement of the state-of-the-art consumption of biodegradable plastics in industry. Initially in this study we focused on the development of toughened PLA/PCL blends. These blends show significant improvement in their thermo-mechanical properties. Elongation at break of samples increased, from 4% to more than 200%, tensile toughness improved for about two orders of magnitude, and simultaneously lower seal and hot tack initiation temperatures obtained, as compared to pure PLA. The depression of seal and hot-tack initiation temperature will make packaging safe and prone to less defects during the process, as the other layers are not distorted at lower sealing temperatures. A lower processing temperature also contributes to the more cost effective processes. Moreover, development of mechanically superior blends, which represent higher tensile toughness, would provide for safer product perspective.

As far as resolving the above-stated challenges is concerned, the change in composition of these blends should be analyzed both through its effect on the morphology of the blends and their thermo-mechanical behavior, which are addressed in the first part of this thesis.

We subsequently looked for an alternative choice for the seal layer production from biodegradable plastics. It is important practically to predict the initial and final operation window of the sealing temperature of the developed resins. This can be achieved by understanding of the change in physical properties of these resins and, more importantly, the crystallinity and crystal content of resins in use. In the second part of this study we showed, how hindrance effect caused

by melt blending of these resins will significantly change the crystal content from about 15% to less than 1% and hence the temperature at which the interfacial diffusion of the molecular chains starts and the entanglements are formed. We designed our blends using the developed knowledge of the effect of the insertion of linear molecules in the structure of olefin-based seal grade resins which have been recently established in our research group and can also be applied for biodegradable resin. Parallel comparison of the molecular behavior gave rise to the development of biodegradable seals with noteworthy improved self-adhesion properties.

Lower crystallinity of blends and the capability of the cast film processing technique to provide a higher available surface of modifying resin are also of great importance, while analysis and control of the morphologies play a significant role in understanding the behavior of these materials. Combining all of the above, results in blends of a lower hot-tack initiation temperature, which are capable of sealing at lower temperatures between 60ºC-70ºC, i.e. 20ºC lower than that of pure PLA. It will provide a wider operational window and significantly higher hot tack strength.

Canada is among the countries with high priorities for environmental safety and it has developed many recycling and composting plants to minimize waste management hazards to nature. Presence of these facilities is a potential opportunity to develop eco-friendly ideas for biodegradable packaging, knowing that the package will end up in an industrial facility which, in turn, can make the best use of it by adding nutrients to the soil rather than doing more damage to it.

Developing a biodegradable product requires the post-use analysis of the effects that processes and techniques used have on the potential of these plastics to be degraded by bacterial activities. Analysis showed that this material is not degrading as a whole homogeneous isotropic plastic. The disintegration studies combined composting with ATR-FTIR techniques revealed that there is a chance of selective degradation of each phase of their blends in a microbial active environment, which required deep understanding as this may result in a non-compostable package outcome.

We had a chance to analyze PLA-based blends beside the PHB-based counterparts owing to the samples provided by Biomer company (Germany), which provide an interesting comparison of the difference between hydrolysable and non-hydrolysable degradation mechanisms in biodegradable blends.

Hydrolysis and degradation of phases were probed by ATR-FTIR analysis and correlated to their CO_2 evolution as a result of composting. This technique was successful in determining the change in the composition and properties of blends through the composting process.

Mechanical tests were combined with detection techniques to obtain practical proof of the capabilities of material selection and process design in tailoring the degradation time for developed biodegradable packages.

CHAPTER 9 CONCLUSION AND RECOMMENDATIONS

9.1 Conclusions

Results obtained in this study showed the potential of biodegradable blends, based on the toughened PLA, to be used as the seal layer in flexible packages. Blending significantly improves the tensile toughness of PLA, and blends of PLA with PCL have shown major improvement in seal characteristics, which are comparable to polyolefin based seal resins. (Najarzadeh et al., 2014) A comparison between the properties of these blends with polyethylene based blends can be found in our previous work. Addition of PCL can affect PLA's elongation at break, while the addition of PCL up to 20% will increase the elongation at break up to 150%. Higher elongations at break are obtained by increasing PCL content. The modulus of elasticity of blends has decreased and the samples show slightly lower tensile strength at 20% PCL content.

Elongational flow field of the cast film process elongates the dispersed phases, and laminar morphology is obtained in developed films. Films are provided with a higher surface area covered with a more flexible PCL elongated phase, which will help increase the interfacial diffusion of polymeric chains and higher entanglement and lower the hot-tack and seal initiation temperatures. Films with a 20% PCL can successfully decrease the seal initiation temperature of the PLA by up to 15 ºC. Decrease of the seal initiation temperature is ample for a seal machine to save more energy through sealing as the seal initiation temperature of these blends falls far below the seal initiation temperature of PE/EVA blends, which are commercially used for food packaging applications.(Najarzadeh et al., 2014) Increase in the content of PCL also increases the hot-tack strength of the blend films up to double, which is almost in the range expected form commercial olefin-based seal resins and have been discussed in our comparative study of biodegradable blends with the polyolefin based counterparts.(Najarzadeh et al., 2014) All the films have been sealed over the melting point of PCL, i.e. 55 ºC, and the films had noticeably high seal strength.

As the interest of this work the preparation of seal layer films from resins with higher melting point than PCL have been studied using aromatic co-polyester resin, PBAT, with melting point of around 110-130 ºC. Removing the crystals formed in film processing by melting of the

films and quenching in liquid nitrogen is shown to be a reliable technique, as negligible crystallinity has been detected in DSC thermograms of quenched films.

Hot-tack initiation temperature of PBAT is significantly decreased by the removal of crystals through thermal treatment, and self-adhesion of amorphous films is noticeably improved. Crystals were shown to act as barrier for chain diffusion, and with the removal of crystals the films' hot-tack initiation temperature decreases up to about 25 ºC. It is a significant decrease in practical applications. Blending of PBAT as minor phase with PLA again shows a significant improvement in toughness and puncture resistance of the films. Blends demonstrated restricted crystallinity and a lesser amount of crystals which is proved to be favorable for seal applications.

The effect of lower crystallinity of blends on increasing the interfacial diffusion of polymeric chains works as opposed to the hindering effect of rigid PLA chains, and a maximized seal initiation depression of about 20 ºC is obtained in blends with 20% PBAT content.

Blending not only affects the physical properties of the obtained films but also their composting behavior as well as time of degradation and disintegration in an active microbial environment.

ATR-FTIR spectroscopy is a powerful technique that allows following the changes in the structure of pure and blend samples through the composting process. The peak area ratio of ATR-FTIR spectrum in the range of 1650 cm^{-1} -1800 cm^{-1} in 50-50 wt% blends of PLA with PBAT and also in 50-50 wt% blends of PHB with PBAT samples has been used as an indication of changes in the composition of these blends through composting time. ATR-FTIR investigation revealed the selectivity of composting to degrade one phase of a blend, i.e. PLA in PLA/PBAT blends and PHB in PHB/PBAT blends to a higher extent, and form a porous 3D network. These 3D networks, observed in SEM images, were shown to become rich in the PBAT phase as the composting proceeds. Formation of these networks explains the retarded disintegration of the blends. The changes in the mechanical properties demonstrate the significant effect of hydrolysis on the softening of PLA samples. Hydrolysis of PLA samples through composting has also been analyzed by the FTIR technique and has been correlated to threshold of CO_2 evolution through composting. As the SEM images reveal, cracks would initiate on the surface of PLA samples at around 10 days allowing for the higher rate of OLAs diffusion to the compost and more bacterial activity.

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9.2 Original contribution

- Biodegradable blends with superior seal and hot-tack performance are developed and analyzed. The mechanical improvement was shown to be resulted simultaneously to make these blends suitable for packaging applications.
- Fundamental study of correlation of crystallinity and hot tack initiation temperature was carried out. The same technique can be applied to many semi-crystalline biodegradable resins to develop sealable blends with an acceptable operational temperature window. The sealing barrier can be removed by using melt blending and quenching to remove crystal structures in binary blends.
- A practical method to follow the degradation behavior of biodegradable resins in the composting process was established by combining ATR-FTIR technique with CO_2 collection columns. By way of this method we successfully analyzed the phase degradation of blends in a composting setup.
- Study of the correlation between degradation of blends of biodegradable material and their mechanical properties has been shown to be possible using the defined method based on the selective phase degradation in composting condition..

9.3 Recommendations

Regarding what has been discussed in previous parts, we have briefed on the gist of what has been done including material selection, development of blends, analysis and correlation of the sealing behavior and material properties, development of the composting setup and study of composting behavior of the blends. The following unexplored aspects are recommended for the continuation of this work and future research:

1. Combining more direct measurement techniques like solid NMR technique and 3D-xray diffraction to follow the type and size of crystals formed in pure and blend material. This will help predict the properties after solidification and sealing process to reveal the cause of shift in the seal initiation temperature compared to hot-tack initiation temperature.

2. Aging of blends at different temperatures will provide a wide range of blends with different crystallinity. These blends can be used to obtain a calibration curve for sealing properties of biodegradable blends vs. their composition and crystal structure.

3. Change in the molecular structure can be followed by means of doping techniques and using deuterated polymeric chains which are detectable in IR imaging techniques or use of the NMR technique in solution state. These techniques provide for the ratio of changes in the molecular structure and can predict the molecular weight distribution of degraded blends.

4. An online gas chromatography can be adapted to be used with the composting setup to minimize the calculation errors and reduce the effect of temperature change on the calculation of evolved CO_2 from composted samples. Use of automatic respirometry can reduce required time for testing significantly as this system can do multiple measurements of different composting vessels online.

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